COAL TAR DISTILLATION

AND

WORKING UP OF TAR PRODUCTS

B-267

BY

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SECOND EDITION
REVISED AND ENLARGED

LONDON
BENN BROTHERS LIMITED
"THE GAS WORLD" OFFICES 8 BOUVERIE ST., E.C.4
1917

PREFACE TO THE FIRST EDITION

CONSIDERING the importance of the coal-tar industry at the present day, it is surprising how few practical text-books there are on this subject. I feel, therefore, that no apology is needed for offering to students, gasworks and tarworks managers, and others interested in this industry, and in chemical technology, a short treatise dealing in a practical manner with the distillation of coal tar and the working up of its chief products.

In order that this book could be produced at a moderate price it has been necessary to deal with the plant and processes used in the working up of the chief products obtained by the distillation of coal tar in a more or less brief manner. Special attention has been given to the plant used for and the process of distillation of tar, as this portion of the industry is the most important, there being many works in which tar is submitted to distillation, or a partial distillation, for special purposes and the distillates sold to other distillers for working up.

As far as possible I have adhered to descriptions of plant and processes with which I have had a practical acquaintance, and I have drawn many of the illustrations in a diagrammatic form in order to render them more easily understood.

With reference to the figures relating to "change over" points, temperatures used, amounts of distillates obtained, and so on, those given have been employed in actual practice at one time or another, but they must be taken as guides only, as coal tar and coal-tar distillates, etc., are liable to variation.

My thanks are due to the firms of Messrs. Thos. Broadbent & Sons, Ltd , S. H. Johnson & Co., Ltd., and Robert Middleton, for their kindness in lending me electros with which to illustrate chapter xiv. Also to Mr W. R. Ball for the great assistance he has given me in reading over much of the manuscript. Thanks are also due to my wife for the assistance she has given me in the preparation of the Index and the correction of the proof sheets.

ARTHUR R. WARNES.

Hull, 1913.

PREFACE TO THE SECOND EDITION

THE excellent reception given to the first edition of this work and the rapidity with which this and a second impression were disposed of has clearly indicated to the publishers and the author that there is a need for a concise text-book on the subject of coal tar distillation; hence a second and revised edition. In offering this to his technical friends, whatever its merits or shortcomings, the author hopes they will find it helpful to them in their works practice or their studies.

On account of its importance and its close connection with the coal tar industry, the subject of gas stripping has been dealt with, an entirely new chapter being devoted to it. It is the desire of the author that this chapter be of material assistance to those who intend to erect a gas-stripping plant, and to gas-engineering students who are preparing for their examinations. Unfortunately, owing to circumstances over which he has had no control, the author has not been able to say all he would like about the plant used in the process of gas stripping. Best thanks are due to Mr John Bond, of Southport, for the trouble he has taken in preparing details and a diagram of his gas-stripping plant, and for his permission to publish them.

Many additions have been made to the majority of the old chapters, some new diagrams have been inserted, and the subjects of continuous dehydration and distillation have received some attention.

Thanks are due to Mr H. P. Hird for particulars relating to continuous dehydration and distillation of coal tar, and for the loan of several electros with which to illustrate the text.

To his esteemed friend, Mr Arnold R. Tankard, F.I.C., F.C.S., the author tenders an expression of his obligation for the many valuable suggestions in connection with the analytical chapter; also for supplying the manuscript relating to the bacteriological testing of disinfectants and to the Berthelot-Mahler calorimeter, and for preparing the table of Road Board specifications.

For the many kindnesses shown to the author by the publishers he offers his expressions of gratitude, and his acknowledgments are due to Dr H. G. Colman for his kind permission to publish his methods for the determination of the percentage of benzene, toluene, and xylene in commerical toluol, and the analysis of crude benzol from coal gas.

The preparing of the manuscript and drawings for the second edition of this work has been done under great difficulties owing to high pressure of work brought about by the great European war, and also to the many duties which the author has had to perform in connection with the Navy and Army Auxiliary Medical Services. In spite of this every care has been taken to avoid the creeping in of errors.

To his wife, who has rendered him valuable assistance in the revising of the Index, the bringing together of new material, and the reading of the proof sheets, the author offers his best thanks.

ARTHUR R. WARNES.

Hull, 1917.

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COAL TAR DISTILLATION

CHAPTER I

Coal tar—its composition—effect of nature of raw material and heat of carbonisation on physical properties and chemical composition of tar—results of practical distillations—coalite tar—vertical retort tar—increasing toluene in tar—"free carbon" of tar

COAL tar is such a familiar material that it is unnecessary to give a description of its appearance. It is a very complex mixture of chemical compounds, chiefly of the aromatic series. The manner in which it is prepared and the nature of the raw material (coal) influence to a wide extent its chemical composition and physical properties. Dealing first with its chief physical constant, specific gravity, this varies in practice between 1.090 and 1.215, according to the temperature of carbonisation or kind of retort employed. The lower-gravity tars are generally produced when low carbonisation temperatures are used, or if the coal is carbonised in chamber or vertical retorts. High heats in horizontal retorts produce tar of high specific gravity. Viscosity is affected in a similar manner. Reference to Tables I and II will illustrate these statements.

TABLE I

	[1] High Heat Tar Horizontal Retorts. Temp. approx. 1100° C.	[1] Low Heat Tar. Horizontal Retorts. Temp. approx. 800° C.	[2] Vertical Retort Tar.	[3] Chamber Retort Tar.
Specific gravity at 60° F.	1.207	1.000	1.10 to 1.12	1.18

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[1] Lewis T. Wright. *Jour. of Gas Lighting*, vol. lii. p. 169.
[2] Higher figure from *Proc. Inst. Gas Engineers*, 1908, p. 130.
[3] *Gas World*, Feb. 26, 1910, p. 262.

TABLE II[1]

	Tar ex English Coal.	
	Viscosity—Engler degrees.	
	Horizontal Retorts	Vertical Retorts.
At 20° C.	550.0	39.3
,, 50° C.	51.0	3.9
,, 70° C.	23.0	2.2
Specific gravity	1.246	1.124

The absolute chemical composition of coal tar is far from settled, and even at the present day comparatively little is known about it. When tar is submitted to destructive distillation upwards of 190 definite chemical compounds can be separated from the distillates and the pitch. Whether they all exist in the tar before it is destructively distilled is not certain. That light products which distil at comparatively low temperatures, such as carbon disulphide, benzene, toluene, xylene, phenol, and also some naphthalene, do exist as such in coal tar is an established fact, but whether the same is the case with all of the higher molecular weight compounds is doubtful. It is probable that some of them are formed by the decomposition of lower molecular weight compounds, and also by condensation (the combination of two or more molecules of the same or of different substances with the separation of water).

A fact to be borne in mind is that the coal tars turned out by the many gasworks in the world vary very much not only in their ultimate chemical composition, but in regard to the percentage and quality of the distillates and the pitch obtained from them when submitted to distillation in a tar distillery. In practice, coal tar on distillation is split up into the following chief fractions:—Ammoniacal liquor, crude naphtha, light oil, light creosote or carbolic oil, creosote, anthracene oil, and pitch, and it is from these that many valuable products are recovered.

It has been proved in practice that the nature of the raw material and the temperature of carbonisation affect the chemical composition, and, therefore, the quality of the tar. Dealing with the first condition, very shaley coal, or cannel coal, produce tars which yield on distillation products containing a large quantity of bodies of a paraffinoid nature. As paraffins are undesirable substances to certain users of coal tar distillates, the occurrence of these bodies will, of course, in such cases lower the market value. Practical working has shown that North Country coal yields a tar which on distillation gives a fairly low percentage of light oils and a rather high yield of creosote, naphthalene, and anthracene, while tar produced from Midland and Yorkshire coals yields on distillation rather more light oils and less creosote, naphthalene, and anthracene; that is if comparative methods of carbonisation and temperatures are employed.

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[1] Dr W. Allner. See *Jour. of Gas Lighting*, July 11, 1911.

With reference to the effect of the temperature of carbonisation on the constitution of tars, it is found that those produced at low temperatures yield on distillation, in addition to phenols of the carbolic acid series, phenols of a different series rather less acid in behaviour and probably of the creosol and guaiacol type. Also, there is a smaller yield of naphthalene and of the benzene hydrocarbons, and a large percentage of hydrocarbons of the paraffin and olefine series. Instead of most of the nitrogen occurring in the form of pyridine bases it appears in the form of aniline and its homologues. The amount of "free carbon" is also small. On the other hand high temperature tars, *i.e.* those produced at high heats of carbonisation of coal, yields on distillation only traces of paraffinoid hydrocarbons, the predominating hydrocarbons being those of the benzene, naphthalene, and anthracene series. The nitrogen occurs principally in the form of pyridine bases, and the phenols consist chiefly of carbolic acid and its homologues. The percentage of "free carbon" is generally high. In the writer's opinion the high percentage of "free carbon" is not due so much to the high heats employed as to the shape of the retort and the amount of free space. This is borne out by the comparatively low "free carbon" content of tars from heavily charged retorts, and the very low "free carbon" content of vertical retort tar. It has been found in practice that tar obtained from heavily charged retorts is of a superior quality to that produced from light charges, in that it is much thinner, contains less "free carbon" and a higher percentage of light oils. This type of tar appears to hold less water in suspension, which is a distinct advantage. Figures[1] on record show that there is a drop in the specific gravity from 1.185 to 1.105. In lightly charged retorts, in which there occurs a good deal of free space, part of the gas and probably some of the tar is "cracked" into lighter materials and "free carbon," and this latter substance to a very large extent is carried up the ascension pipes and arrested by the tar in the hydraulic main. Table III illustrates this and gives other useful information.

[1] *Jour of Gas Lighting*, October 12, 1909.

TABLE III[1]

	Tar from		
	Works using high heats and light charges. Per cent.	Works using moderate heat and fairly heavy charges. Per cent.	Continuous Vertical Retorts. Per cent.
Water	2.0	2.0	2.0
Light oils	1.0	6.0	5.6
Carbolic and creosote oils	14.0	32.0	41.4
Anthracene oil	5.0	4.0	4.0
Pitch	78.0	56.0	47.0
"Free carbon" in pitch	36	17.0	5·5

The average results of some practical distillations made by the writer, using Yorkshire, Northern, and Midland tars, are given in Tables IV, V, and VI.

TABLE IV

	Yorkshire Tar.		Northern Tar.[2]	
	Gallons per ton tar.	Per cent. by weight.	Gallons per ton tar.	Per cent. by weight.
Ammoniacal liquor	1.8	0.82	25.10	11.5
Crude naphtha	10.5	4.36	2.20	0.9
Light oil	12.3	5·43	6.70	3.0
Creosote	53.5	24.81	33.60	15.6
Anthracene oil	6.0	2.92	21.40	10.4
Pitch	11.5 cwts. per ton	57.80	11.60 cwts. per ton	57·5

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[1] E. G. Stewart, *Trans. Lond. and Southern District Junior Gas Assn.*, 1911-12, p. 43.

[2] A very watery type of tar.

TABLE V

MIDLAND TAR

	Gallons per ton tar.	Per cent. by weight.
Ammoniacal liquor	4.50	2.06
Crude naphtha	4.36	1.82
Light oil	18.20	8.20
Middle oil	9.20	4.26
Creosote and anthracene oil	31.80	15.10
Pitch	12.90 cwts. per ton.	64.50

TABLE VI

ULTIMATE PRODUCTS FROM MIDLAND TAR

90's benzol	1.85	gallons per ton
90 per cent. at 160° C.	3.10	,, ,,
Heavy naphtha	0.75	,, ,,
50's carbolic	3.75	,, ,,
Cresylic	3.40	,, ,,
Pyridine bases	0.30	,, ,,
Creosote	55.25	,, ,,
Pitch	13.20	cwts

When considering the low temperature tars the fact that they contain paraffinoid bodies should not be overlooked. Coalite tar is a member of the class of tars containing these bodies. This tar varies in specific gravity between 1.050 and 1.070; it contains practically no "free carbon" or naphthalene, and the first products of distillation are very volatile. It is these distillates which contain the paraffin bodies, and from the tar distiller's point of view render the tar valueless. It should find use as a fuel oil, or if sufficient volume can be obtained to warrant separate storage and distillation, the lighter distillates could be employed, after rectification, for motor spirit and the heavier distillates for fuel oil. Table VII gives the results of two analyses of coalite tar.

TABLE VII

(a)[1] COALITE TAR (b)[2]

Specific gravity	1.07
	Per cent.
Below 170° C.	10.8
170°–270° C	20.0
270°–350° C	30.0
Pitch	39.2

Specific gravity	1.075
	Per cent. by vol.
Water	2.64
Up to 170° C	3.10
170°–225° C	13.72
225°–240° C	8.35
240°–270° C	8.35
270°–300° C.	8.80
300°–320° C	12.31
	Per cent. of tar.
Pitch	40.00

Unfortunately, vertical retort tar exhibits the same fault as coalite tar in that it contains paraffinoid bodies. On this account it is not possible to prepare from it suitable benzol and toluol from which to manufacture pure benzene and toluene and their derivatives. From an inspection of Table VIII it will be seen that the specific gravity of this tar and also the "free carbon" content are very low. On distillation, compared with coal tar from horizontal or inclined retorts, it yields a smaller percentage of benzol and toluol, very little phenol, and practically no naphthalene. The pitch is of a finer quality than that obtained from horizontal or inclined retort tar, in that it is brighter and contains very little free carbon.

TABLE VIII

VERTICAL RETORT TAR (DESSAU)

Specific gravity	1.084
	Per cent.
Free carbon	1.06
Volatile in pitch	77.7
Specific gravity of pitch	1.19

	Per cent. by weight.
Ammoniacal liquor	4.40
Up to 170° C.	3.75
170°–270° C.	33.60
270°–350° C.	8.00
Pitch	48.25

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[1] *Gas World*, May 5, 1909, p. 654.

[2] Prof. Lewes (see *Chem. Trade Jour.*, Dec. 23, 1911, p. 633).

VERTICAL RETORT TAR (GLOVER-WEST CONTINUOUS)[1]

Specific gravity	1.074		Per cent. by weight.
	Per cent.	Water	1.3
Free carbon	3.40	Light oils to 170° C.	5.0
Pitch	very soft	Carbolic oils to 230° C.	16.0
		Creosote oils to 270° C.	8.9
		Anthracene to 310° C.	7.9
		Pitch	60.9

At the time of writing (1917) the subject of increasing the yield of toluene from tar is receiving a great deal of attention on account of the importance of this material in the manufacture of munitions of war. One of the most interesting investigations in this connection is that of G. Stevenson,[2] who finds that the mixing of limestone with coal prior to charging into the retorts increases the yield of toluene from the tar obtained. Some of the results he secured are set out in Table IX.

TABLE IX

QUANTITY OF TAR TAKEN, 9000 C.C.

	Normal carbonisation with "C" washing.	Limestone used, No "C" washing.	Limestone used and also "C" washing.
Crude naphtha	176 c.c.	320 c.c.	508 c.c.
Middle oils	720 c.c.	850 c.c.	800 c.c.
Toluene in tar, lbs. per ton of coal	0.27	0.41	1.01

From time to time "free carbon" has been a subject of interest and speculation as to its composition. The result of many qualitative experiments has caused the writer to come to the conclusion that this material is not pure or elemental carbon, but a mixture of this material with other bodies of a high carbon content. This conclusion is supported by the work of Hubbard and Reeve,[3] who have made several ultimate analyses of "free carbon" with the results shown in Table X, and also by the work of J. M. Weiss.[1] The result of an analysis of average "free carbon" from coal tars made by this worker is given in Table XI.

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[1] D. Fulton, *Gas World*, March 13, 1915, p. 298.

[2] *Gas World*, January 29, 1916.

[3] *Proc. Am. Soc. Testing Materials*, ii. (1911), 665.

TABLE X

	From	To
Carbon . . .	90.17	94.26
Hydrogen . .	2.59	3.31
Oxygen . . .	1.81	5.91
Sulphur . . .	0.50	1.78

Nitrogen—no trace upon a qualitative test.

TABLE

Works Samples fron

Conditions.
Horizontal retorts.
Two ascension pipes, charges 5¾ cwts. in 6 hours, 1800° Fahr. .
Two ascension pipes, charges 6½ cwts. in 6 hours, 1950° Fahr. .
Two ascension pipes, charges mostly 12 cwts. in 12 hours, 1900° Fahr.
One ascension pipe, charges 9½ cwts. in 8 hours, 1950° Fahr.. .
Inclined retorts.
One ascension pipe, charges mostly 6 cwts. in 6 hours, 1900° Fahr.

Jour. Indust. and Eng. Chem. vol. vi. No. 4, p. 279, April 1914.

TABLE XI

Carbon	89.85
Hydrogen	3.30
Nitrogen	1.10
Oxygen	3.13 (by difference)
Sulphur	1.28
Mineral ash	1.34

The inference drawn by Weiss from many of his experiments is that the solvents used actually enter into combination with some of the constituents of the tar, and that the longer the time allowed for the solvents to act the larger the amount of compound formed and the greater the amount of insoluble residue (" free carbon ") obtained.

In a paper read before the Scottish Junior Gas Association Dr Davidson[1] gave some interesting figures dealing with the variation in the composition of tar according to the kind of retort and the carbonising temperature employed. These figures will no doubt be found useful for the purpose of comparison, and they are reproduced in Table XII. The figures are reckoned on the dry basis.

XII

Sales Tanks

Specific Gravity.	Free Carbon. Per cent by weight.	Percentage by volume.						
		Up to 100° C.	100° to 130° C.	130° to 170° C.	170° to 230° C.	230° to 270° C.	270° to 330° C.	Above 330° C. (Pitch).
1.182	16.4	1.4	1.9	0.3	14.7	9.5	11.3	60.9
1.191	20.3	2.1	1.3	0.1	12.5	10.8	8.1	65.1
1.129	13.9	2.0	0.6	0.4	18.9	12.8	13.6	51.7
1.200	20.2	1.5	0.7	0.8	12.7	11.1	8.5	64.7
1.176	19.4	2.0	0.7	0.4	15.1	11.2	11.4	59.2

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[1] "Tar and Liquor." See *Gas World*, April 18, 1914, pp. 523-7.

TABLE

Coal Test Plant

Conditions.
Horizontal retorts.
Coal " A " (Derbyshire)—
(1) Coalite conditions
(2) Ordinary conditions, 6.4 cwts. in 6 hours,
Coal " B " (Yorkshire)—
(1) 4.54 cwts. in 6 hours, 1640° Fahr
(2) 4.87 cwts. in 6 hours, 1975° Fahr.
Light and heavy charges.
Coal " C " (Derbyshire)—
(1) 6.41 cwts. in 6 hours, 1980° Fahr
(2) 12.21 cwts. in 12 hours, 2065° Fahr.
Coal " D " (Derbyshire)—
(1) 6.52 cwts. in 6 hours, 2020° Fahr.
(2) 9.59 cwts. in 9 hours, 1980° Fahr.
Coal " E " (Derbyshire)—
(1) 6.49 cwts. in 6 hours, 1990° Fahr.
(2) 13.41 cwts. in 12 hours, 1990° Fahr.
Wet and dry mains.
Coal " F "—
(1) Wet main, 6.41 cwts. in 6 hours, 1980° Fahr.
(2) Dry main, 6.51 cwts. in 6 hours, 1980° Fahr.
Coal " G "—
(1) Wet main, 6.41 cwts. in 6 hours, 1920° Fahr.
(2) Dry main, 6.35 cwts in 6 hours, 1965° Fahr.
Poor and rich coals.
(1) Derbyshire, 6.23 cwts. in 6 hours, 1990° Fahr.
(2) Yorkshire, 6.49 cwts. in 6 hours, 2025° Fahr.
(3) Wigan cannel, 5.74 cwts. in 6 hours, 2040° Fahr.
Dessau vertical retorts.
(1) Coal " H " (Yorkshire)
(2) Horizontals for comparison, 6.44 cwts. in 6 hours, 2070° Fahr.
Woodall-Duckham vertical retorts.
(1) Coal " I " (Derbyshire)
(2) Horizontals for comparison, 6.41 cwts. in 6 hours, 1910° Fahr.

XII. *(continued)*

Experiments

Specific Gravity.	Free Carbon. Per cent. by weight.	Percentage by volume.						
		Up to 100° C.	100° to 130° C.	130° to 170° C.	170° to 230° C	230° to 270° C.	270° to 330° C.	Above 330° C. (Pitch)
1.120	7.0	3.7	3.2	0.1	18.1	10.9	13.2	50.5
1.190	19.1	1.5	1.5	0.4	10.9	10.7	10.3	64.7
1.160	..	12.7	2.1	1.6	4.8	16.1	12.5	50.2
1.234	27.5	3.5	1.1	0.8	7.9	7.3	7.6	71.8
1.190	19.1	1.5	1.5	0.4	10.9	10.7	10.3	64.7
1.150	15.9	1.9	1.6	0.4	17.1	11.4	15.5	52.1
1.211	23.8	1.7	2.7	0.0	8.9	10.0	7.7	69.0
1.151	15.5	3.9	3.2	1.4	11.1	10.2	11.5	55.7
1.177	20.5	2.4	5.1	0.3	13.2	12.0	7.8	59.2
1 ·07	..	1.6	0.8	0.1	21.7	11.0	14.2	50.6
1.190	19.1	1.5	1.5	0.4	10.9	10.7	10.3	64.7
1,210	27.7	0.7	0.6	0.5	8.0	9.1	5.2	75.9
1.158	18.9	2.9	0.7	1.2	14.5	9.8	11.8	59.1
1.215	26.8	1.0	0.9	0.4	8.6	8.7	10.2	70.2
1.190	24.6	1.4	0.9	0.2	12.2	10.3	10.9	64.1
1.229	28.4	1.6	1.0	0.3	10.2	9.1	7.9	69.9
..	11.4	4.6	3.9	1.4	5.2	8.9	4.6	71.4
1.14	4.47	0.6	0.4	0.4	12.0	10.7	13.1	62.8
1.216	25.8	1.7	1.4	0.1	10.0	9.2	7.9	69.7
1.110	3.8	1.7	2.9	0.5	12.[illegible]	11.8	8.6	62.3
1.190	19.1	1.5	1.5	0.4	10.9	10.7	10.3	64.7

In Table XIII will be found some figures relating to tar obtained from Woodall-Duckham vertical retorts.

TABLE XIII

Distillation of Tar obtained from Woodall-Duckham Vertical Retorts[1]

	No. 1. Moderate heats. Per cent.	No. [illegible] Higher heats. Per cent.
Up to 100° C.	1.5	0.6
100—130	1.0	1.8
130—170	2.2	0.4
170—230	11.4	16.2
230—270	17.5	14.2
270—330	18.0	15.7
330—350	12.4	6.9
350—370	12.0	9.0
Pitch	24.0	35.2

The writer considers the figures given by Tooby for the pitch are rather too low. On the practical scale distillation is stopped at a temperature varying between 310° and 320° C., whereas in the table the residue above 370° C. has been taken as pitch.

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[1] Chas. F. Tooby: "Notes on the Working of the Woodall-Duckham Installation of Vertical Retorts at Windsor Street, Birmingham." M. J. G. Assn.: *Gas World*, Jan. 24, 1914.

CHAPTER II

How tar is received from gasworks—tar tips—storage of tar—construction of storage tanks—pumps—tar mains.

TAR is delivered to the distillers from the gasworks in railway tank waggons, lighters or keels, tar carts, and, less frequently, the distillery is connected direct to the source of supply by a pipe-line. Examples of the last named are to be found in London, Birmingham, and some other towns. Consideration will not be given here to the construction of the tank waggons and the other vehicles of transport, beyond stating that cylindrical tank waggons are the best to use for tar carriage. A few words, however, on the plant and methods employed for emptying them on their arrival at the distillery is necessary.

It is usual to provide a tar-tip into which these vehicles can be emptied prior to running or pumping the tar to storage tanks, but it should be mentioned that in some cases the tar is run direct into an underground tar storage tank or tar well. The tar-tip for railway tank waggons may be constructed between the railway metals or on the side of the permanent way, but the latter position is perhaps the better both from the point of view of safety and convenience. A spot should be chosen at a suitable part of the works siding, and, of course, the position should be one which will allow the waggon to pass over a weighbridge first. A hole of sufficient size should be dug between the metals and the bottom well puddled with clay. A covered wrought-iron tank, well coated with a bituminous iron protective solution on the outside and provided with a 14-inch diameter hole and cover, is lowered into the excavation, the sides and top well puddled, and the earth filled in on the top to the sleeper level. The tank may be built of brindled or Staffordshire blue bricks set in cement, or of reinforced concrete, and in both cases the excavation should be well puddled first.

In the writer's opinion a wrought-iron tank is the easier to put in and the more suitable for this particular work. The tank capacity should be at least that of a large railway tank waggon; and the writer would add in this connection that he has used with economy, and to great advantage, the tank portions of old railway tank waggons after they have been overhauled. It is, of course, necessary to provide an outlet for the tar and to connect this outlet up to a pump. In the case of old railway tank waggons the discharge outlet can be conveniently used, or, if desired, this can be closed, and an outlet cut in one of the sides of the tank near the bottom. As the tar gets very thick in cold weather it is an advantage to use tank waggons provided with a steam coil and to see that a steam main and suitable connections are rigged up near the tip. Warming up the tar will expedite the process of emptying considerably. As many tank waggons are not fitted with a steam coil, arrangements should be made so that a flexible steam-pipe can be inserted into the tank on its arrival. This is done by connecting to the steam rig a piece of 1-inch or 1¼-inch flexible metallic tubing of sufficient length to allow a foot or two to rest on the bottom of the tank, or else using 1-inch to 1¼-inch steam-pipe, employing the necessary elbows and bends to render the piping flexible and to allow it to adapt itself to the position. Unfortunately, open steam is forced into the tar, and this means that it will become mixed with a certain amount of condensed water. Also there is some risk of noxious vapours escaping from the manhole of the tank: covering this with sacking will minimise this trouble.

The tip for a tar cart can be constructed in a similar manner to that just described. If it is desired to put in a small tank care should be taken to see that it holds rather more than the volume contained in the cart (approximately 270 gallons), and as to its position, it is advisable to place it as near the emptying pump as possible.

To empty keels and lighters it is necessary to run a pipe line to the canal or river side, and fit suitable flange connections at the end, to which a flexible suction pipe may be attached. The flexible portion may be of wire-bound leather or flexible steel tubing (the latter is the better); and the internal diameter of this and the pipe line should not be less than 4 inches—6 inches is preferable.

There are works in existence which pump the tar as received direct into the stills, but this is a plan much to be deprecated, and, of course, in large works one which could not be adopted. The chief reasons why tar should be stored are (*a*) to allow much of the entangled liquor (ammoniacal water) to separate, and thus reduce the period and expense of distillation, and (*b*) to keep a sufficient stock in the works to enable it to be run during the "low make" season at the various gasworks from which the supply is drawn. It must be obvious that storage tanks should be of large capacity, and there are tanks now built to hold as much as 1,000,000 gallons. They are constructed above and below ground, and in the latter case are often known as wells.

Storage tanks erected above ground are, if built of wrought-iron or mild steel, cylindrical in form, or if constructed of reinforced concrete, cubical or rectangular solid in shape. Those built below ground are generally constructed of brick or reinforced concrete, and may be cylindrical, rectangular solid, or cubical in shape—the two last-named kinds being the general rule.

As these tanks are required to hold a very considerable weight of material, often upwards of 3500 tons, it is necessary that a site be chosen where the strata is firm, and that a good foundation be put in. If the nature of the strata is not known, it is advisable to make one or two borings at the chosen site. In the case of underground tanks these borings should be carried to a depth greater than that of the depth of the tank and its foundation; for it is quite possible that the ground for some 15 feet or 20 feet below the surface may be quite firm and then a few feet beyond this running sand or slippery clay may occur. In cases of this nature, if it is not possible to put the storage tank in another position, special precautions must be taken when building the foundation. Should the tank be constructed of brick, concrete, or reinforced concrete, and the foundation built on unsuitable strata, no precaution being taken for this state of affairs, an unequal settling may take place and produce cracking, the results of which would be serious. If the tank is built of iron and subjected to the same unsuitable conditions the straining produced by unequal settling would bring about leaking at the seams. On firm ground the concrete foundation need not be more than 18 inches thick. In cases where spongy ground has to be built upon, it is advisable to increase the thickness of the concrete and reinforce it with small section angle, tee, or aitch iron, arranged in lattice form. This makes a kind of concrete raft, which will practically do away with all risk of unequal settling.

It is very advisable to build the sides of concrete tanks on the reinforced principle. They may be built on the Monier system, in which expanded metal or wire network formed of iron wire is arranged so that the thickest are placed longitudinally and the thinnest transversely, or on the Hennebique system, in which round iron bars are employed; in both cases, of course, the metal-work is surrounded by concrete. The sides of the tank may vary between 9 inches and 18 inches in thickness, according to whether the tank is below or above ground level, or to the size of the tank. One of the best mixings of concrete to use is 4 : 2 : 1 (G. E. Davis recommends 7 : 3 : 1), and it is very necessary that the materials be thoroughly mixed, that an excess or insufficiency of water is avoided, and that the aggregate is free from clay or loam. The wet concrete should be thoroughly punned, best with a pointed rammer, and the moulding boards should not be removed until the concrete is thoroughly set. It is absolutely essential that no tar (or creosote) be put into a concrete tank until it is quite set, and a period of several months should be allowed to elapse before putting the tank into use. If a concrete tank is constructed properly it will withstand a liquid pressure of 8½ lbs. per square inch without leaking. The inside of the tank should be rendered with neat cement. It is advisable to puddle round the sides of concrete tanks that are built below ground before filling in the earth. The top of the tank may be constructed of reinforced concrete, wood, or iron plates.

If it is desired to build the tank of bricks, those of a non-absorbent type, such as brindled or Staffordshire blues, must be employed. The bricks should be set in cement, and the joints should not be too thick, about 3/16 inch, and the tank must not be put into commission before the cement joints are thoroughly set. As the walls are being built up, good puddle should be well rammed round the outer side to a thickness of at least 12 inches. The thickness of the wall should be between 14 inches and 18 inches, and it is advisable to render the inside of the tank with about ⅛ inch of neat cement. The top of the tank may be built of similar materials to those used for concrete tanks. Iron tanks are sometimes placed below ground, and if this is done it is essential that every care be taken in the riveting and caulking of the seams. It is wise to apply a good thick coat of pure bitumen paint, free from sedimentary matter, to the underside of the bottom and to the outsides of the tank. A concrete foundation should be made at the bottom of the excavation, the thickness of which will depend upon the condition of the ground underneath. Properly made clay puddle should be rammed round the sides before filling in the earth, and the tank may be covered in with a wood or iron roof.

Reinforced concrete and iron tanks are the two kinds usually built above ground, and as the method employed in the construction of the former is the same as for those placed below ground, no further description is needed. The fact that they must be stronger must not be lost sight of. It is desirable, however, to consider briefly the construction of iron tanks. These tanks may be built to contain as much as 1,000,000 gallons, but a very usual size is between 250,000 and 400,000 gallons. As these tanks are erected in the open air, and, therefore, exposed to all conditions of weather, corrosion troubles will rapidly set in if they are not properly covered on the outside and underside of the bottoms with a pure bitumen paint free from sediment. The under side of the bottoms should be covered during erection, and the outsides after completion. It is absolutely essential that good sound work be put into the tanks during their erection, as from the time of completion they are generally full, or partly full, of tar, and this condition will make it exceedingly difficult, if not impossible in many cases, to carry out repairs without first emptying—a very awkward state of affairs to crop up, say, at a busy time.

In all cases the seams should be double riveted and thoroughly caulked. Care should be taken that the rivets are not too short. They should be of sufficient length to allow the riveter to snap the tail of the rivet properly, and the height of a finished snap-head should be about three-quarters the diameter of the shank. Mild steel rivets of a good quality should be used; poor quality steel rivets are apt to fracture. Rivet holes should be drilled for preference; in punching holes there is a great risk of an unseen fracture occurring between one hole and another, a condition which may lead up to a serious leak when the tank is put into commission.

The sheets of mild steel of which storage tanks are built should be, for preference, pressed into shape, and their thickness should vary, being greater for those plates which are to form the bottom ring than for those it is intended to use for the top and intermediate rings. The bottom plates need not be quite so thick as those of the bottom ring. As an example of the thickness of the various plates used in building a tank, the following will prove useful.

The tank is required to hold approximately 300,000 gallons of tar, and in this case the diameter may be 55 feet and the depth 20 feet. A tank of this depth would be built up of four rings, each being 5 feet in width. The thickness of the plates composing the bottom ring should be $\frac{5}{16}$ inch, the plates of the next ring $\frac{9}{32}$ inch, the next $\frac{1}{4}$ inch, and the plates of the top ring $\frac{7}{32}$ inch. A thickness of $\frac{1}{4}$ inch is quite sufficient for the bottom plates. The bottom angle ring should be constructed of $2\frac{1}{2}$ inches by $2\frac{1}{2}$ inches by $\frac{3}{8}$ inch section angle steel, and the top angle ring of 2 inches by 2 inches by $\frac{1}{4}$ inch section angle steel. Double riveted joints, with the rivets having a pitch of 2 inches, are used throughout.

Many tanks are not covered, but if a cover is desired, it can be constructed of mild steel sheets of $\frac{1}{8}$ inch in thickness, with the exception of the crown plate and the outer circle of plates, which should be of $\frac{3}{16}$ inch. The cover is generally supported by a middle stanchion, on the top of which are riveted radial arms reaching to the circumference of the tank. Two hatches about 3 feet square, provided with *light* cast-iron covers, should be put in the cover on the outer circle plates, and provision will also have to be made for the entry of the tar inlet pipe, and an outlet for air and foul gas. This outlet pipe should be connected to a small purifier box to retain sulphuretted hydrogen, etc.

If the storage tanks are not covered, it is usual to keep about

18 inches of water on the top of the tar to prevent nuisance. It is necessary, however, to remove the water several times during the year, and as it will contain a certain amount of ammonia it shoud not be run to the drain, but sold as weak ammonia liquor to an ammonia works, or in the event of the tarworks possessing an ammonia plant worked up in this. The tar inlet pipe should be so constructed that it reaches about two-thirds the way down the tank. This will avoid agitation of the top liquor and splashing during pumping, when the tank contains a considerable amount of tar. Of course this precaution need not be taken if the tanks are covered. The inlet pipe should be of wrought-iron and of a diameter of either 4 or 6 inches. With regard to the outlet pipe for removing the tar the centre line of this should be about 9 inches from the bottom of the tank. This pipe can be made of cast-iron, or better of welded wrought-iron, and should be about 6 inches in length and of a diameter of 6 inches. It is carefully riveted to the tank and fixed by means of a flange to a best quality cast-iron plug-cock. If preferred a sluice valve can be used in place of a cast-iron plug-cock, but all the fittings must be of iron.

It is a great advantage to provide storage tanks with 2-inch wrought-iron steam coils. They should be put in in the form of a gridiron and supported on rollers. A good method of putting the inlet and exhaust of these coils through the tank side is shown in Fig. 1. The advantage of a steam coil is felt during the winter months, when tar, if it is cold, becomes very difficult to pump, owing to its increased viscosity.

As it is an exceedingly difficult matter to dip a tar tank in order to find accurately the amount of tar and weak ammoniacal liquor it contains, it is advisable, in order to check the dips, to insert a series of ½-inch pet cocks up the side of the tank at a pitch of 3 inches, commencing about 1 foot from the bottom of the tank and finishing about 6 inches from the top.

Some care should be exercised in choosing tar pumps. They must be strong, of cast-iron throughout to minimise corrosion, and fitted with either piston or mitre valves. For delivery into storage tanks, the charging of stills or preheaters, or general transport of tar from fairly long distances, pumps having a 6-inch delivery should be installed. There are several suitable types of pump on the market. Of them may be mentioned three of which the writer has had experience: these are, the Worthington, Tangye, and Evans' Cornish. Each of these three makes gave satisfactory results in working, but the writer has no doubt that other makes would prove as suitable. It must be remembered that the pump must be fitted with cast-iron rams or plungers, or ring packed buckets; leather or canvas packed buckets are not suitable.

It is a wise plan to employ pipe lines of at least 6 inches in diameter for the conveyance of tar, and they are best constructed of cast-iron socket and spigot pipes. The joints must be made with care or else trouble will occur from leaks.

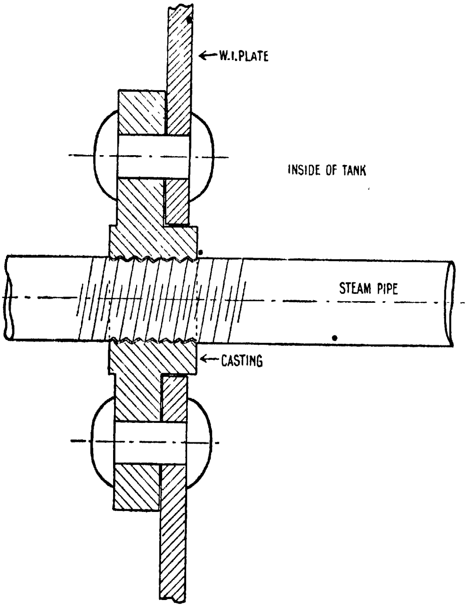

FIG. 1.—A Method of inserting Steam Pipe into Storage Tanks.

Properly made lead-wool joints will give highly satisfactory results both from the point of view of saving money and securing tightness. Another good joint is obtained by using the turned and bored socket and spigot pipe of the Liverpool pattern, but it should be remembered that this type of joint is not suitable in situations where the pipe lines wind: lead joints will have to be used in these cases.

CHAPTER III

PLANT USED IN THE DISTILLATION OF TAR

Tar stills—metals used in their construction—design—fittings—building of still—safety contrivances—swan neck—swan-neck stool—steam-pipes—charge block—dipping cock—manhole and lid—tail pipe and pitch cock—thermometer.

IN a tar distillery the pieces of plant subjected to the greatest wear and tear are tar stills, and very careful consideration should be given to the design and construction of these pieces of apparatus. The portions of a still above the pitch level at the finish of the operation are more or less severely corroded by ammonium chloride and to a lesser extent by ammonium sulphide.[1] The corrosion is much more severe if the still dome, manhole, and charge pipe inlet are wrongly designed, or not properly lagged. The other part of a still which often gives much cause for anxiety is the bottom, which, if not properly built or protected, or if the fireplace is wrongly constructed, may "come down" in a few weeks after being put into use.[2]

In the construction of tar stills, wrought-iron, mild steel, or sometimes cast-iron is used. To employ cast-iron is, in the opinion of the writer, a great mistake. Although it is now possible to make very large castings in which blowholes are practically absent, freedom from this weakness does not render the metal suitable, as there are other faults. For instance, the thickness of a cast-iron still is much greater than that of one constructed of wrought-iron or mild steel, the average of the sides and top being 1½ inches, while the bottom varies between 2 and 2½ inches, the latter thickness occurring at the junction of the run-off pipe (see Fig. 2). This greater thickness of metal not only means a much heavier weight to support on the brick seatings, but a greater fuel consumption. Assisting the thickness of metal in bringing about the latter drawback is the somewhat poorer heat conductivity of cast-iron as compared with wrought-iron. Then the uneven thickness of the bottom, at the place just mentioned, combined with the comparatively poor expansive properties and low tensile strength, opens up the risk of cracking. The writer has experienced this trouble,

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[1] See "Corrosion of Industrial Iron Work," by A. R. Warnes and W. S. Davey, *Journal of Society of Chemical Industry*, June 15, 1910. The *Gas World*, April 23, 1910, p. 528, and May 7, 1910, p. 599.

[2] See "Coal Tar Distillation," by A. R. Warnes; *Trans. Midland Junior Gas Association* for 1910, pp. 15-29, or the *Gas World*, October 15, 1910, p. 462.

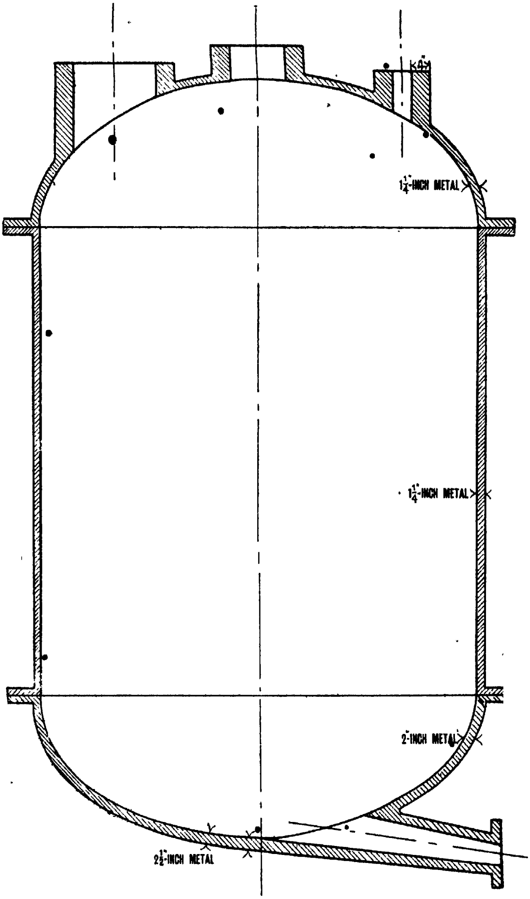

FIG. 2.—Diagram of Cast-iron Tar Still (not to be recommended).

which is of a very serious nature. In this connection it should be pointed out that it is practically impossible to repair satisfactorily a cracked cast-iron bottom, and therefore it has to be scrapped—no small matter, as it means the removal of much brickwork before the damaged bottom can be got away and a new one put in its place. Then there is the rebuilding of the brickwork after the repair is finished. It will be noticed on inspecting the diagram (Fig. 2) that flanged joints are used in the building up of the still. This is a most unsuitable kind of joint for a vessel that is subjected to such high temperatures as a tar still. The chief difficulty is to keep the joint tight, even when the faces are perfectly trued up. The risk of a leaky bottom joint is increased somewhat by the fact that the thickness of the metal of the bottom is greater than that of the sides, thus producing a certain amount of unequal expansion and contraction.

Both mild steel and wrought-iron enter largely into the construction of tar stills, but there is a diversity of opinion as to which is the better metal to use. It seems, however, that mild steel is in greater favour. Whichever metal is chosen, it is very necessary to see that the best quality is obtained. In the case of wrought-iron, there is always the risk of laminations or blisters occurring, even in the best qualities, and the thicker the plates the more liable they are to this defect. The writer has frequently seen plates which to all outward appearances seemed perfect open out very badly on shaping, owing to lamination defects. Fracture is frequently caused by laminations or blisters, and corrosion is materially assisted. Owing to the fact that wrought-iron is brought into contact with fettling materials in the course of its manufacture it is not homogeneous in structure, and this state is one which also assists corrosion. Some prefer wrought-iron because of its fibrous structure, but this condition must not be considered as an absolute indication of strength. In cases in which shaping has to be done across the grain, there exists the risk of cracking.

Mild steel is in the writer's opinion the better metal to use. It requires, however, rather more care in working the plates. Well made mild sheet is perfectly homogeneous in structure, owing to the fact that in the process of manufacture the whole mass is in the state of fusion. There is a greater freedom from impurities, and the tendency to corrode locally is reduced on this account. Mild steel is rather more ductile than wrought-iron, and, therefore, is more amenable to the treatment received in the process of cambering, flanging, etc.

Much care is necessary in the process of shaping steel plates, and where possible this should be done by hydraulic pressure. When this cannot be done, and of course it is not possible in the case of repairs carried out in a tar distillery, careful attention must be given to the heating of the plates, and in particular to the shaping of them. The plates should be first heated to redness and then beaten into shape with wooden mallets, using cast-iron templet blocks. Metal hammers must not be employed under any circumstances. Research into the causes of corrosion has proved that hammering iron or steel renders it more liable to attack. This is brought about by the production of local strain, and when metal hammers are used this condition is set up to a greater extent than when the plates are shaped with wooden mallets. It has been discovered that over-heating renders iron or steel more liable to corrosion, the amount of corrosion product being on an average 20 per cent. more from over-heated metal than from metal normally heated.

All rivet holes should be drilled and countersunk on the inside, not punched, thus avoiding the risk of cracking between one hole and another, and also the setting up of local corrosion when the still is in use. A research undertaken by T. Thickens showed that corrosion took place to a greater extent around punched rivet holes than around those which had been drilled, owing to the local shearing strain set up by the punch, and the writer has been able to confirm this worker's results. It is also policy to use rivets made of the same metal as the plates, and they should be of ample length, to allow a good snap-head to be formed. The seams must be properly caulked, as lack of attention to this detail will lead to a number of very troublesome leaks. Machine riveting gives better results than are obtained by hand, and it is also more economical. It should be employed whenever possible. With reference to the diameter of the rivets, and the pitch of the rivet holes, these dimensions should vary according to the thickness of the plate used. A good thickness to employ, at least for the shell, and the one generally adopted (sometimes throughout), is $\frac{1}{2}$ inch. The pitch of the rivet holes and diameter of the rivets should be 2 inches and $\frac{7}{8}$ inch for wrought-iron and 2 inches and $\frac{15}{16}$ inch for mild steel. The centre of the rivet hole to the edge of the plate should be $1\frac{5}{16}$ inch for wrought-iron and $1\frac{3}{8}$ inch for mild steel. As the top, or dome, of the still is subjected to the action of corrosive vapours to a greater extent than the shell, and with some tars very much more so, it is advisable to construct this portion of the still of slightly thicker plates than those used for the shell. A useful thickness is $\frac{9}{16}$ inch; the pitch of the rivet holes and the diameter of the rivets should be $2\frac{1}{8}$ inches and 1 inch respectively for mild steel and $2\frac{1}{8}$ inches and $\frac{15}{16}$ inch for wrought-iron. The centre of the rivet hole to the edge of the plate should be $1\frac{1}{2}$ inches for mild steel and $1\frac{7}{16}$ inches for wrought-iron. The writer strongly recommends the use of mild steel for the construction of the dome and shell of the still.

It is difficult to say definitely whether wrought-iron or mild steel is the best kind of metal to use for constructing the still bottom. The writer has had a case in which two still bottoms, one of mild steel, one of wrought-iron, and each put into commission at the same time, have "come down" within a week of each other, necessitating the replacing of the greater part of the bottom of both stills. The conditions in this instance were certainly very drastic, the tar being of a very bad quality and the still bottoms not protected in any way by brickwork. The writer's experience (bearing in mind the case just mentioned) has caused him to come to the conclusion that, on the whole, wrought-iron is the better metal to use. Careful observation has shown that wrought-iron bottoms, properly treated and protected by brickwork when necessary, last longer than those constructed of mild steel. An investigation commenced by the writer, part of which is not completed, seems to show that metal of fibrous structure is the best kind to use for the construction of still bottoms. In all cases where a still bottom has "come down," cracked, or become badly burned, the metal removed from the damaged parts has been highly crystalline in structure, and very brittle, even when fibrous metal (wrought-iron) has been used. Experiments have shown that this crystalline state takes some time to form in the case of wrought-iron; mild steel is already of a crystalline nature. It appears that the crystalline state is brought about mainly by the iron taking up carbon, and it is quite well known to metallurgists that the greater the carbon content of the metal the more brittle it becomes. Brittleness is a source of weakness in a still bottom in many ways, and the writer has known cases in which still bottoms have been cracked, and even pieces knocked out, during the process of still cleaning. A good thickness of wrought-iron plate to use for still bottoms is ⅝ inch, and for this thickness rivets of 1 inch diameter are necessary. The pitch of the rivet holes should be 2¼ inches, and 1½ inches is allowed from the centre of the rivet hole to the edge of the plate.

Tar stills are built in various sizes, the chief being, 10, 15, 20, and 30 tons working capacity. The 15-ton size is used very largely in this country, a great point in its favour being that its contents can be worked off in between 14 and 15 hours. Although tar stills of various shapes have been tried from time to time, none of these shapes has proved so satisfactory in use as that known as the pot or vertical still, and it is this type of still that will now be described. The pot still is divided into three chief parts, namely: the shell, which is a vertical cylinder the diameter of which is a little greater than the height; the top or dome, which, in a properly designed still, should have very little rise in it; and the bottom, which is concave from the outside and pitched high. The still is provided with the following fittings: A safety-valve, or similar contrivance; a swan neck for conducting away the vapours; a steam-pipe inlet block, and a steam-pipe inside connected to a perforated coil or criss-cross arrangement; a charge block, for connecting up to the charging pipe; a dipping cock; a manlid stool and lid; and a tail pipe, with cock, for running off the pitch. A thermometer pipe is sometimes fitted either into the dome or the top of the swan neck. The separate parts of the still and the several fittings will now be dealt with *seriatim*.

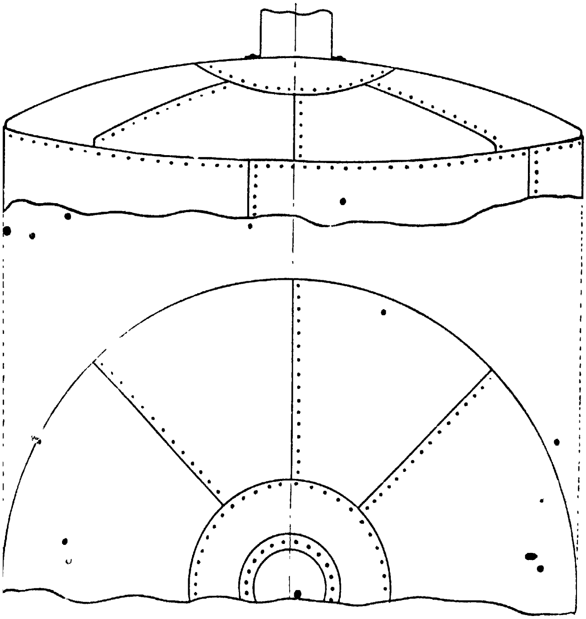

FIG. 3.—Diagram showing a Method of arranging Sketch Plates on Still.

The shell of the still is built up of wrought-iron or, better, mild steel plates, riveted, and of thicknesses already described. For a 12-ton still the diameter of the shell may be 9 feet and the height 8 feet 6 inches; for a 15-ton still, diameter 9 feet 6 inches and height 8 feet. The dome, or top, of the still is constructed of sketch plates and a dome plate (see Fig. 3), riveted and of thicknesses previously described. The number of segments or sketch plates varies according to the size of the still or the ideas of the designer; for instance, in a 12- or 15-ton still this number may be eight. The pitch or rise should not be more than 15 inches for a 12- or 15-ton still. A large number of stills have been and are at present constructed with high pitched domes; this is a mistake, as it does not add to the efficient working of the still, nor is it necessary from the point of view of strength, and it materially assists in the process of corrosion. As pointed out by the writer in a paper read before the Society of Chemical Industry,[1] corrosion of tar stills is brought about by aqueous vapours containing chiefly ammonium chloride in the dissociated state, and proceeds most rapidly at those points where condensation takes place, and where the condensed vapours are able to trickle down the plates. A high-pitched dome provides all these bad points; it is more difficult to lag properly, it exposes a greater surface to the cold atmosphere, especially of winter (most tar stills are in the open), and the manhole is in a position which further assists in the condensation and temporary retention of the condensed vapours, which eventually trickle down the plate on the underside of the hole. Cases have come under the writer's notice in which the plate under the manhole has been corroded through three times in five years, and in all cases of high-pitched domes he has noticed

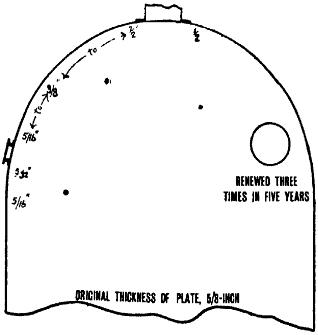

FIG. 4.—Diagrammatic Illustration showing Extent of Corrosion which can take place on a High-pitched Dome.

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[1] *Journ. Soc. Chemical Industry*, June 15, 1910, No. 11, vol. xxix.

a large amount of grooving on the inside. Fig. 4 illustrates diagrammatically the extent of corrosion which can take place on a high-pitched dome. The correct type of dome to use is shown diagrammatically in Fig. 3.

The still bottom should be constructed of wrought-iron plates, of a thickness already described, and these plates must be well riveted and properly caulked. Sometimes still bottoms are constructed in one piece, but this is not a good plan; it makes repairs more costly and the bottom is not so strong. The most satisfactory way is to construct the bottom of a number of segments, or sketch plates, united at the crown by a circular plate known as the crown-plate. The number of segments may vary between 8 and 12. Methods of arranging these and the crown plate are shown diagrammatically in Figs. 5 and 6.

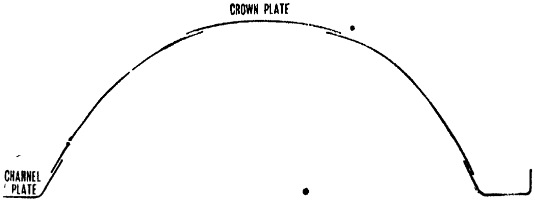

FIG. 5.—A Method of arranging Plates for Still Bottom (Diagrammatic).

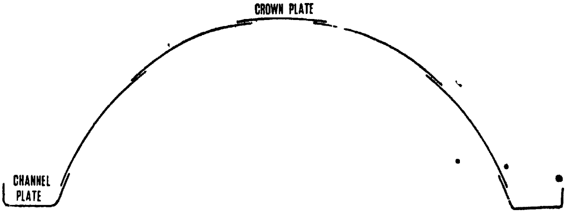

FIG. 6.—A Method of arranging Plates for Still Bottom (Diagrammatic).

The diameter of the crown plate varies between 2 feet 6 inches and 3 feet. It is advisable that the rise or pitch of a still bottom should be as great as possible. For a 12- or 15-ton still the rise should be 2 feet 9 inches, and for a 30-ton still 3 feet 6 inches. The bottom is joined up to the shell in two ways; (*a*) by angle iron, and (*b*) by means of what are known as channel plates.

The latter method is the better. Figs. 7 and 8 show diagrammatically the two methods. Important points to bear in mind when constructing still bottoms are the necessity of securing as complete a draining off of the pitch as possible, and to avoid the introduction of joints, which increase the tendency of the pitch to lodge and ultimately coke. Joints which make the work of still cleaning difficult should also be avoided. The angle-iron joint possesses the defects just mentioned, the nearness of the rivets acting as a nucleus for deposits which eventually coke (see Fig. 7). If channel plates are used, however, the risk of these troubles occurring is much minimised, and one of the best types of channel plate to adopt is shown in Fig. 8. It is not advisable to make butt joints when connecting up the channel plates ; lap joints are the best.

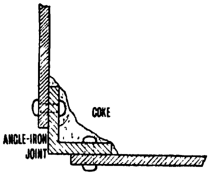

FIG. 7.—Angle Method of joining Bottom of Still to Shell.

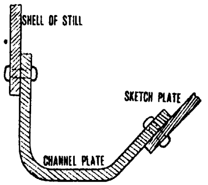

FIG. 8.—Channel Method of joining Bottom of Still to Shell.

The advantages of building a high pitched bottom to a still are, (*a*) a large heating surface is secured, (*b*) the metal can contract and expand with comparative ease, thus minimising strain, (*c*) the stiffness of the bottom is increased, (*d*) the draining off of the pitch is materially assisted.

When a tar still is working normally, there should be very little pressure inside, but should a stoppage occur in any portion of the condensing worm, a serious pressure may be set up. In order to give warning that a stoppage has occurred, and at the same time relieve abnormal pressure, a safety-valve, or a similar contrivance, must be fitted to the still. Safety-valves of the dead-weight type are the best to use. The valve should be designed with as shallow a casting as possible on the vapour side of the seat in order to avoid a stoppage by solidified anthracene or naphthalene salts. A type of valve designed by H. Astbury and the writer, which in practice has given excellent results, is shown in Fig. 9. The safety-valve stool should be cast as shallow as possible, and riveted on to the still dome (see Fig. 10). The seat should not be too narrow, and the valve should be weighed to blow off at a pressure of 6 lbs. to the square inch. Another contrivance often known as the S-pipe is illustrated in Fig. 11. This device is nothing more than a water seal, the two limbs of the U-bend being filled with ordinary water. The length of each limb should be 3 feet 9 inches and the internal diameter of the tube ¾ or 1 inch. There is a much greater risk of this safety contrivance becoming clogged than with the safety-valve just described; the clogging, of course, taking place in the upright tube. The S-tube may be fitted to the top of the swan neck, or on the still dome.

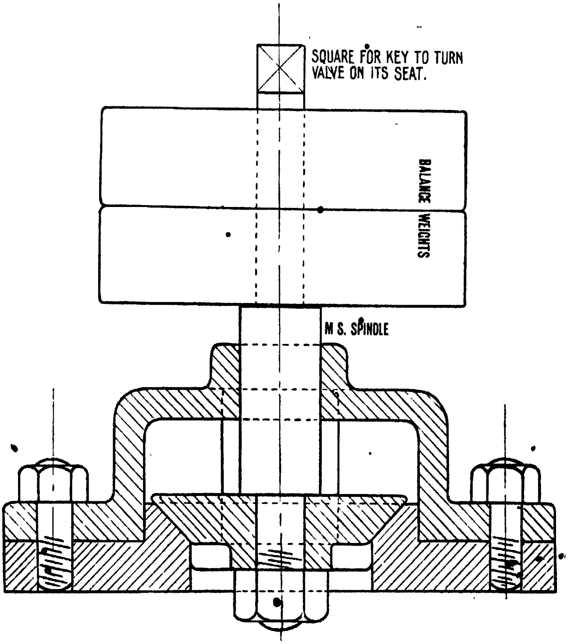

Fig. 9.— A Type of Tar Still Safety-valve.

The swan neck should be made of cast-iron, and is bolted on to a swan-neck stool (see Fig. 12). Cast-iron is used because it is easier to manufacture a fitting of this shape in that metal, and it also resists to a far greater extent than wrought-iron or mild steel the corrosive action of some of the tar distillates. The internal diameter of the stool should be 12 inches and the swan neck tapers from 12 inches down to 4 inches. A flange must be cast on the narrow end for the purpose of attaching it to the condensing coil. The swan-neck stool should have cast on to it a short length of about 4 inches beyond the lower flange, which will project into the still when the stool is riveted into position. This will prevent any condensed vapours from trickling down the inside of the dome, and so assist in minimising the rate of corrosion of the plates of the dome.

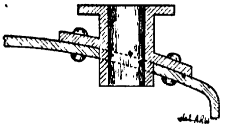

FIG. 10.—Safety-valve Stool.

For the purpose of reducing the temperature towards the end of the tar-distilling operation, and to keep the still contents in a state of agitation, in order to prevent as far as possible the coking of the pitch on the bottom-plates, it is necessary to provide the still with open steam coils. At the point where steam enters the still, it is necessary to fit a steam-pipe inlet-block, which is made of cast-iron, and of a design shown in Fig. 12. It is just as well to provide two valves on the steam main in order to reduce the risk of a leakage of condensed steam into the still, should one valve become defective (see Fig. 12), and it is not a bad plan to introduce a small pet cock between the two valves, through which any condensed water may be blown before the steam is admitted into the still. Fig. 12 illustrates this. The steam inlet pipe may be of 1 inch or 1¼ inch internal diameter. This pipe is connected inside the still to one of a similar diameter, and of such a length that it reaches the crown plate of the still bottom. Here it is coupled up to a 4-, 6-, or 8-way piece. Into the outlets of these fittings, pieces of perforated pipe, bent to conform to the shape of the still bottom, are fitted. The internal diameter of these pipes should be about ½ inch, and the holes should be drilled in such a position that the steam, as it emerges, impinges upon the plates of the still bottom. The pitch of the holes should be 6 inches, and they should be drilled on each side alternately, an occasional one

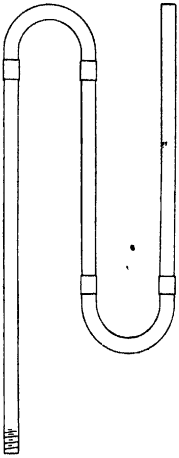

FIG. 11.—S-Pipe Safety Contrivance: used instead of a Safety-valve.

eing placed right underneath. The end of each steam-pipe hould, of course, be closed by a plug or cap. As regards the

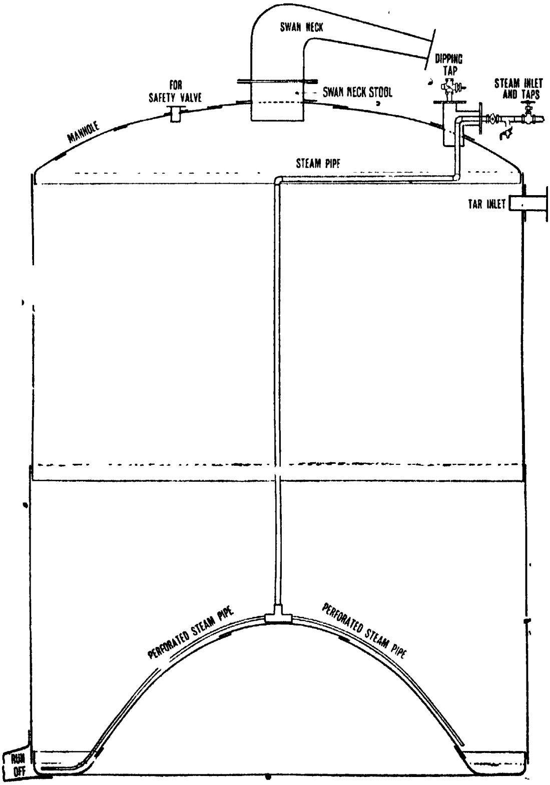

FIG. 12.—Diagrammatic Illustration of Tar Still.

engths of the perforated pipes, these often have to be determined by a working experience with the still into which they re put. It is often found that coking will take place to a greater extent on one part of a still bottom than another, and sometimes even in the trough or channel, and when this occurs it is necessary to arrange that jets of steam play upon these parts. Several methods of arranging these pipes are shown diagrammatically in Fig. 13.

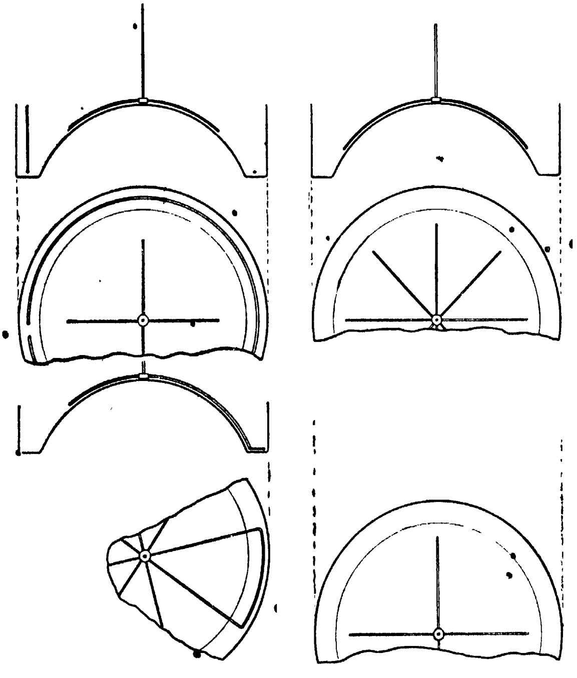

FIG. 13.—Arrangement of Steam pipes.

To couple up the charge pipe to the still, a casting often termed a charge block is provided. This fitting is riveted on to the still, either just below the point from which the still top or dome springs, or just above that point on the dome itself. Of the two positions the latter is the better, in any case so far as minimising corrosion is concerned. In the writer's experience, with inlets fitted to the still side there has always been serious corrosion. A good type of charge block and two methods of fitting it to the still are shown in Fig. 14.

In order to prevent overcharging, the still should be fitted with a dipping cock or an overflow tap. The latter is preferred by some; and if it is desired to fit it to the still, it should be placed at the full-charge level. An arrangement for carrying away any tar which may overflow should, of course, be provided. If the still is charged from a preheater, or a blow-boiler which contains an exact still charge, then an overflow tap is not necessary. It is contended by some that a dipping tap is unnecessary; but, particularly in the case of stills charged by preheaters, it is advisable to use this fitting, as there is a possible chance of the charge pipe between the preheater and the still becoming stopped, and the use of the dipping tap provides a ready means by which the stillman can find out that the still is charged and also approximately check the volume of tar in the still. The dipping tap may be an ordinary 1-inch cast-iron plug-cock, and it is advisable to rivet it to the still by means of a flange. A combined steam inlet and dipping tap block is shown in Fig. 12. The dipping rod can be made of narrow flat bar iron. For an overflow cock some prefer to use a 1-inch brass or gun-metal bib-cock, but as these metals are so easily corroded by H_2S, NH_4Cl, etc., it is, in the writer's opinion, best to use cast-iron gland cocks for this purpose.

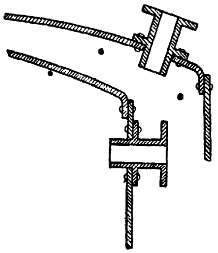

FIG. 14.—Diagram showing Methods of fitting Charge Blocks to Still.

In order that men may enter the still for cleaning purposes, conducting repairs, and making inspections, it is necessary to provide the still with a manhole and a lid to cover it. As there is an element of danger to the workman while he is inside the still, it is advisable to make the manhole rather larger than the regulation size employed by boilermakers. The reason for this is that should a man become "gassed" and have to be hauled out of the still at the end of a rope, great difficulty would be experienced in dragging the man through a regulation size manhole, and in cases like this rapidity of action is of the utmost importance. Oval manholes of 18 inches by 12 inches could be used with advantage.

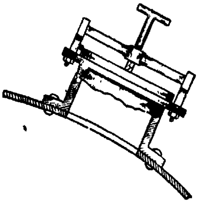

FIG. 15—Manhole and Lid, Wrong Type.

It is a common practice to construct manholes as shown in Fig. 15. This is an expensive and also unsatisfactory design. Owing to the large amount of surface exposed to the cooling influence of the atmosphere, excessive condensation takes place in the casting, and the condensed vapours trickle down the side of the still. This brings about excessive corrosion. There are cases which have come under the writer's notice of still plates having an original thickness of $\frac{5}{8}$ inch being corroded through in eighteen months. The best type of manhole and lid to employ is shown in Fig. 16. This design enables the stillman to cover the manlid completely with lagging, for instance a silicate cotton mat, after he has drawn the manlid tight. There are no projecting surfaces, and even if lagging is not used, the risk of

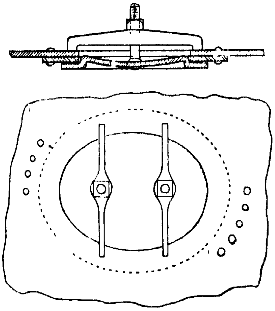

FIG. 16.—Draw-up Manlid, Correct Type.

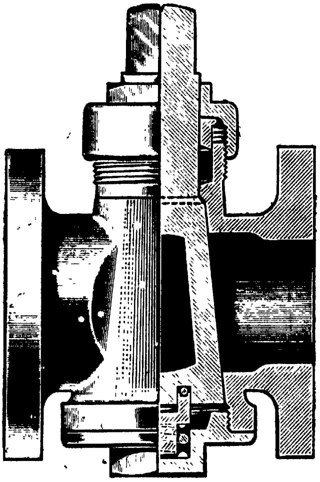

FIG. 17.—Butterfield Cock.

condensation is very much less than if the type shown in Fig. 15 is adopted.

The tail-pipe or run-off pipe should be constructed of wrought-iron or mild steel, and should be riveted to the still casing and channel plate. One example of how this is done is shown in Fig. 12. The portion attached to the still must be carefully flanged, and the rivet holes drilled, *not punched.* It may be 4 inches or 6 inches in diameter, and not less than 18 inches long, and should be provided with a flange, welded on, in order to connect it with the run-off cock. The run-off tap may be of the main cock or Butterfield type (Fig. 17), and the plug should have a full-way. In the experience of the author cast-iron gland cocks do not give such satisfactory results. It is advisable to place an expansion joint between the cock and the pipe which connects it to the pitch cooler.

In this country thermometers are not often used with tar stills, but should it be desired, it is advisable to enclose the thermometer in a case or tube. The tube may be constructed of wrought-iron, welded at the bottom, and a few holes drilled at that point. The top portion should be provided with a flange, by means of which it is riveted to the still dome. It should be placed as near the swan-neck stool as possible. The thermometer is of course provided with a collar, so that it can be screwed into the tube and thus prevent the escape of vapours.

CHAPTER IV

PLANT USED IN THE DISTILLATION OF TAR (*continued*)

Still foundations—settling—ash-pits—fireplaces—settings—curtain arch —flues—burners for gas firing—gas sewer—coal *v.* gas firing.

It is important that tar still foundations should be good solid ones. Before erecting a single tar still, or a battery of them, careful consideration must be given to the choice of a site. If not already known, the state of the ground should be examined, and if it is found to consist of soft gravel, moving sand, or soft, wet clay, then the position should be rejected: compact gravel or hard, dry clay are the best to build upon. On good solid ground of this description a foundation made of properly prepared concrete, and of a thickness between 6 inches and 9 inches, will be found quite suitable. It should be borne in mind that in cases of foundation building it is as well to err on the side of safety, and should there be any doubts as to the state of the natural foundation, a thicker concrete foundation, or one made of reinforced concrete, should be put in. Although cheaper, lime concrete must never be used, and cement which has become damp should be studiously avoided for concrete making. Due regard must be paid to the time taken for cement concrete to set: if, after a lapse of twenty-four hours, it is found to be soft, the lot should be pulled out and replaced by a better make. Every endeavour should be made to avoid excessive settling of a tar still, for if this takes place, many difficulties will subsequently arise. The making of a satisfactory joint between the swan neck and the condenser coil will not be possible, the incomplete draining away of the pitch from the still, and serious cracking of the flues, are some of the troubles which will be brought about.

To a very large extent the efficient working of a tar still depends upon the care used in the designing and building of the flues and the setting of the still. Bad designing and careless building will result in one, several, or all of the following troubles: (*a*) An excessive consumption of fuel; (*b*) a prolonged operation, resulting in extra labour, expense, etc.; (*c*) boiling over at the commencement of the operation; (*d*) burning of the still casing; (*e*) increased corrosion, owing to unequal heating producing strain or to severe heating of plates not covered with liquid;

(*f*) bringing down or burning out of the still bottom. As much attention should be paid to fuel economy in connection with tar stills as with steam boilers. It is quite possible in a large works to burn per annum 600 tons of coal over and above the normal quantity, should the flues be improperly built. This is no small item.

The flues and the fireplace should be constructed of the very best firebrick and fireclay; easily fused firebrick will cause no end of trouble if used. Those bricks having a melting-point of about 3000° Fahr. are the best to employ. For outside work, a non-absorbent brick must be used, and brindled or Staffordshire blue bricks prove very satisfactory in this case. The object of using this type of brick is to prevent the absorption of moisture

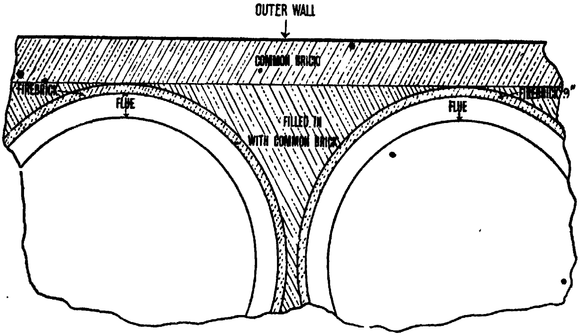

FIG. 18.

during rainy weather, for if this takes place, serious cracking of the brickwork will inevitably follow. In a battery of stills the spaces between the outside of the flues and the straight edge of the outer wall (see Fig. 18) should never be filled in with grouted broken brick or concrete, but should be built in properly with common brick set in ordinary mortar. The mortar should not be laid too thickly between the bricks, either for the inside or outside work: a thickness of $\frac{3}{16}$ inch is ample. This remark applies also to the fireclay used in setting the firebricks. The firebricks must be clean and free from dust before laying, and if very dry they should be moistened with water, otherwise the fireclay will not adhere properly to them. The writer recommends pointing the outside work with neat cement, and covering that at the top with cement rendering roughed with a little sand. The object of roughing is to minimise the risk of the stillman and his assistants slipping when walking on the still top. It is advisable to build the top brickwork with a slight fall towards the edge and to put in an overhanging coping of round or bull-nose bricks (see Fig. 19).

The thickness of the ordinary brickwork outside the flue should be at least 18 inches. In the case of a single still, this brickwork may be built round the flues, forming a cylinder. It is necessary to strengthen the brickwork by encircling the same with straps or bands made of flat bar iron. The brickwork of a battery of two or more stills will remain in excellent condition, and not develop serious cracks, etc., if strengthened by means of buckstaves and tie-bars.

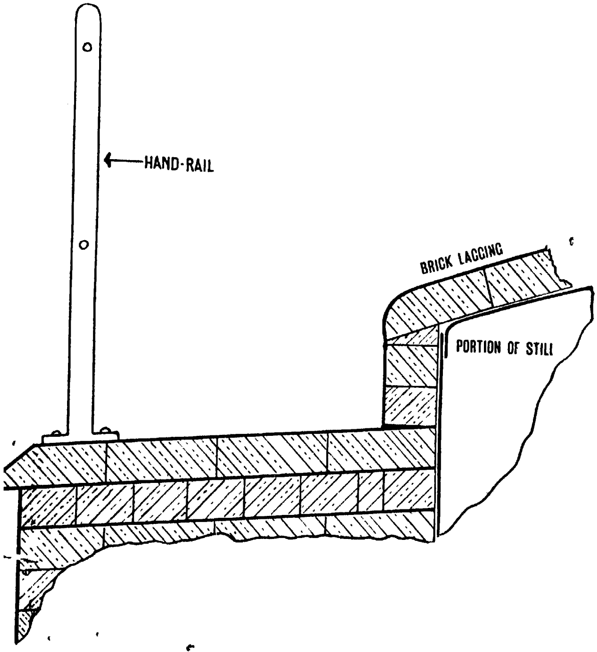

FIG. 19.—Brickwork of Still Top with Coping.

The structure from the concrete foundation to the under portion of the floor of the combustion chamber is built of ordinary brick. It is necessary, however, to build the floor of the combustion chamber with firebrick. This kind of brick is also used to build the still seating, and, of course, the flues. In the lower portion of the structure, an opening is left for the ash-pit, the floor of which should be, for preference, on a level with the ground. Some tar distillers prefer to build the ash-pit below ground, but in the writer's opinion this method is not so safe as the former, should the still bottom spring a leak, and the ignited tar commence to run rapidly into the ash-pit. It is much easier to put out a fire with sand in the case of an ash-pit

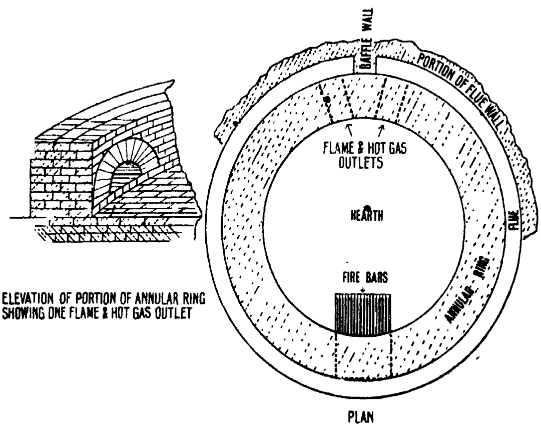

FIG. 20.—Annular Ring (Still Seat) Outlets to Flues.

built on the floor level than one built below ground. The firebars are of that pattern employed for burning small coal (slack or smudge), and are supported on bearing bars and provided with a dead plate, as usual. A cast-iron door frame is built in and arched over during the building of the front portion of the external brickwork.

The still is supported on an annular ring of firebrick, built several courses high, and sprung from the floor of the combustion chamber (see Fig. 20). At a point opposite the fire door position, openings are left for the purpose of allowing the passage of flame and hot gases to the flues. The portions of the channel plate of the still over these openings in the annular ring must be very carefully protected by building small brick arches under them (see Fig. 22), otherwise the metal will soon suffer severely. With reference to the size of these openings, they will vary according to the dimensions of the still, one 9 inches from the base to the top of the arch rise by 1 foot 6 inches wide will prove large enough for most purposes. In between the top of the arch rise and the channel plate of the still at least 12 inches of firebrick should be built. It is advisable in most cases to protect the bottom of the still with a firebrick arch, known technically as a curtain arch. This arch is sprung from the annular ring just referred to (see Fig. 22), and is of course built of the best quality of firebrick. The arch should be built in such a fashion that it provides approximately 4½ inches of brickwork against the still bottom. Some tar distillers prefer to leave a small air space between the firebrick and the still bottom; the writer can recommend this method in cases of bad tar.

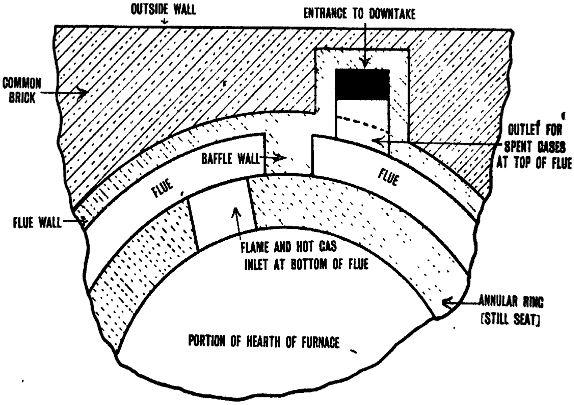
OUTSIDE WALL
ENTRANCE TO DOWNTAKE
COMMON BRICK
OUTLET FOR SPENT GASES AT TOP OF FLUE
BAFFLE WALL
FLUE
FLUE
FLUE WALL
FLAME AND HOT GAS INLET AT BOTTOM OF FLUE
ANNULAR RING (STILL SEAT)
PORTION OF HEARTH OF FURNACE

Fig. 21.—Diagrammatic Representation of Gas Inlet and Outlet in Single Wheel Flue (plan).

In order that the pitch can be run off readily and the still drain well it is necessary to place the still on its seat with a fall towards the tail or run-off pipe. This may be approximately ½ inch to the foot or, say, for a still of 9 feet 6 inches in diameter, 4½ inches. The run-off pipe and cock are liable to become "set-up" with a plug of cold pitch at times, especially during cold weather. To avoid this trouble as much as possible this appendage to the still must be protected from draughts and cold air. This is done by building in the greater part of the tail pipe and constructing a brickwork recess to cover the run-off cock. Into the recess, and covering the cock, a quantity of sand is placed before commencing the distillation. Should by any unlucky chance the cock become "set-up," then a little cotton waste saturated with creosote can be placed under it and ignited, and the heat from the combustion will melt the pitch and set the cock free.

Of the several types of flue, that known as the wheel flue is the best. This kind of flue is built single or double according to the size of the still: a single flue being used for small stills up to

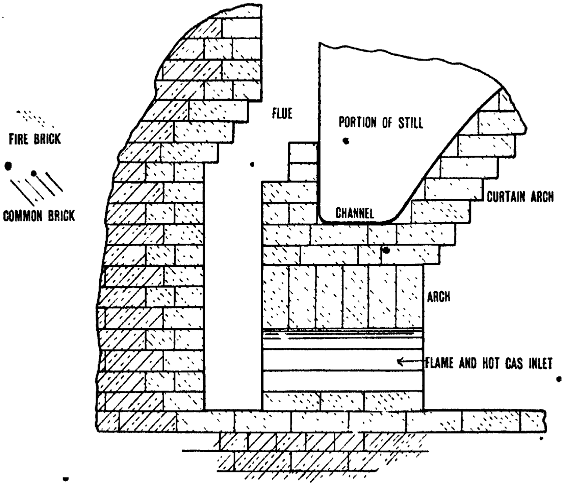

FIG. 22.—Diagram showing one Method of protecting Bottom of Still Shell, also Channel Plate and Bottom.

15 tons, and double flues for the larger sizes. In the case of double flues two openings must be built in the still seat instead of one, in order to split the hot gases and send them in opposite directions round the bottom of the flue. These openings need not be quite so large as that of the hot gas exit of a single wheel flue. Immediately above the arch over the firebars a 9-inch mid-feather or baffle wall is built to the total height of the two flues. On each side of this mid-feather an opening is made in the lower flue cover, in order to allow the hot gases to pass into the upper flue, the mid-feather causing the gases to flow in two directions towards the back of the still, where they come to the downtakes, which in turn lead to the main flue. A damper is

always fitted in the downtake to regulate the combustion of the fuel. The top flue is covered in by overstepping several courses of firebrick, or using firebrick flue covers, *i.e.* slabs of firebrick known as burrs. Tar still flues are generally built 9 inches or 12 inches wide, and of a depth varying with the size of still.

In a single wheel flue the mid-feather or baffle wall must be built in between the gas inlet to the flues and the downtake, in order to cause the hot gases to encircle completely the still (see Fig. 21). The width of the flue may be the same as that of the double wheel flue, and it is covered in in a similar manner. Whether double or single wheel flues are built, it is advisable to protect the bottom portion of the still shell with a few courses of firebrick when very bad tar has to be worked. In order that this may be done it is necessary to recess the outer bottom portion of the flue. Fig. 22 illustrates the manner in which this is carried out. To secure the most satisfactory result the firebrick lining of the flues should be built of circle bricks of the required radius. These can be made to order, and may be obtained from any responsible firebrick manufacturer.

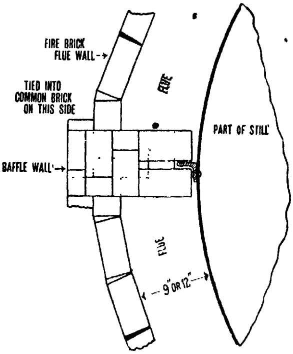

FIG. 23.—Diagram showing a Method of keeping Flue Tight at Baffle Wall.

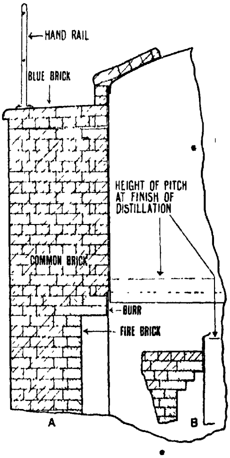

FIG. 24.—Two Methods of covering in Flues: A, with Firebrick Burr · B, by Corbelling.

In building the flue, it should be remembered that the still shell will expand and contract throughout each operation. There is on this account always a certain amount of difficulty in keeping the various parts of the flue tight. In the case of the mid-feathers or baffle walls this may be overcome almost completely by riveting a piece of angle iron to the still, and building the firebrick on both sides of the projecting portion, as shown in Fig. 23. As regards the top cover of the flue, there is less difficulty here, owing to the number of courses of brick built above it and the manner in which the top of the still is covered (see Fig. 24). Only skilled furnace builders should be employed to erect the furnaces and flues; ordinary bricklayers, as a rule, are not sufficiently conversant with this kind of work, and will generally turn out an unsatisfactory job.

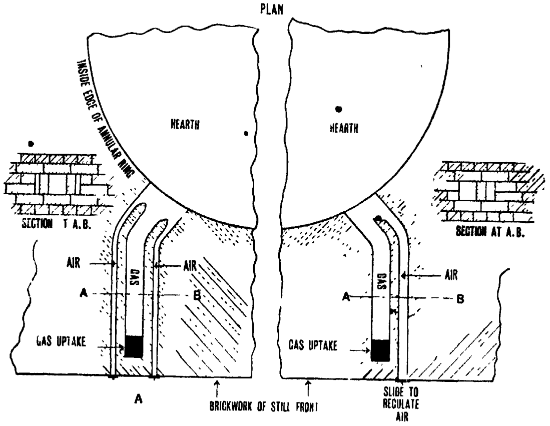

FIG. 25.—Diagrams A and B showing, in Plan, Two Methods of building a Producer Gas Burner of Brick.

If it is desired to employ gas for firing, careful attention must be given to the design and building of the gas and air inlets, passages and burner. Ignition of the gas should not take place until it has reached the combustion chamber, and the air and gas should mix just before they enter that place. The volume of air and gas is controlled by valves, slides, or dampers, and the gas is admitted to the burner passage from the gas sewer or main gas flue by a mushroom valve, controlled by a spindle and wheel. Both the gas and air passages are built of firebrick throughout, and, of course, will run parallel to each other.

Water-air gas is generally forced into the gas sewer from the producer, and is therefore hot when it reaches the gas-burner. The air is warmed a little during its passage to the burner end by the hot bricks with which it comes in contact. Two methods of building a producer gas burner are shown in Fig. 25. The ordinary firegrate is not dispensed with: it is useful in case the gas supply fails, and sometimes as an auxiliary. If desired, a Terbeck or Cumberland burner may be employed instead of using the burners just described. Figs. 26 and 27 will give a general idea of these pieces of apparatus. The firing of tar stills is dealt with on pages 46 and 47.

After the still settings are finished sufficient time should be allowed for the brickwork to dry out. If "green" brickwork is heated a deal of steam is generated and this, due to expansive force, brings about cracking, sometimes of a serious nature, which will eventually lead to a weakened structure and leaky flues. It is wise to allow one or two months to elapse, according to existing conditions, before starting up the fire, the damper being kept open all the time in order that a current of air can pass through the flues and assist in drying the brickwork. A few days before starting the still it should be charged with tar and a slow fire lighted in the grate and kept going for two or three days.

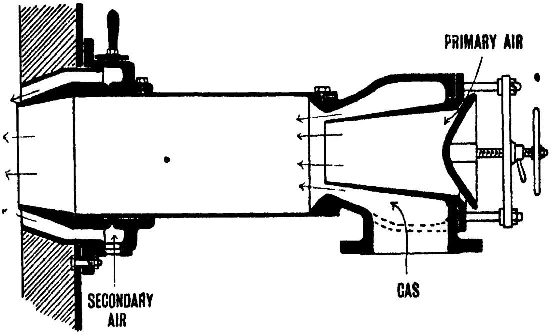

FIG. 26.—Mixing Tube of Terbeck Gas-fired Furnace.

The gas sewer is built below ground, along the whole range of stills, and careful brick setting is necessary in order to avoid leakage of gas. The outside brickwork should be of best blue brick, and the joints made of cement mortar, and not too thick. The lining is built of firebrick, properly tied into the outer wall.

The sewer is covered in with a semicircular arch of firebrick internally, and blue brick externally. It is advisable to provide the sewer with several inspection holes about 18 inches by 2 feet 6 inches in size, covered with cast-iron lids.

Several advantages are secured by the use of producer gas for firing tar stills, among which may be mentioned: (*a*) The operation of distillation may be controlled somewhat more easily; (*b*) the risk of prosecution for making black smoke is obviated; and (*c*) fewer men are required to work a battery of stills. A little more coal is burned per ton of tar if producer gas is the fuel employed, but the cost of this is not so great as that for extra labour if the furnaces are coal fired. For instance, an experiment made on a battery of tar stills run twenty times on coal fires and twenty times on gas fires, using producer nuts as the fuel in both cases, gave the following average results:—With gas firing consumed 1.32 cwts. coal per ton of tar distilled, and with coal firing 1.16 cwts. coal per ton of tar distilled. The extra cost for coal when using producer gas ap-

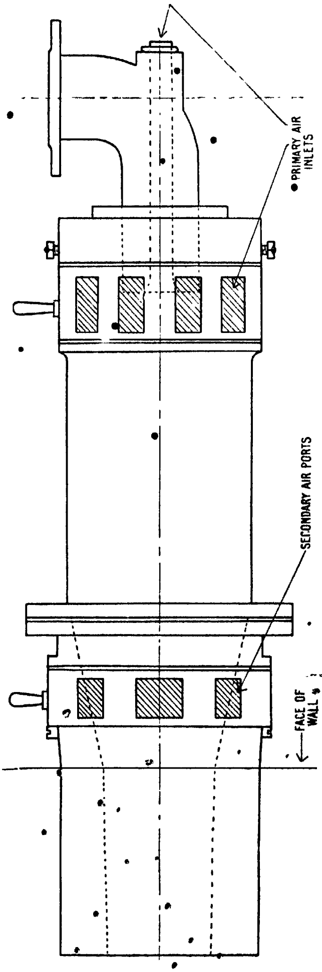

Fig. 27.—Cumberland Patent Standard Producer Gas-burner.

proximated 0.48d. per ton of tar distilled, while the extra cost for labour when the furnaces were coal fired approximated 0.84d. per ton of tar distilled.

It is convenient in this place to say a few words on the subject of still firing. As with steam boilers, the firing of tar stills should receive strict attention in regard to fuel economy. It is an easy matter to secure poor efficiency with either coal or gas firing, even if the still settings are of the first order, if the still fireman is careless in the way in which he manipulates his coal fire or his gas-burner.

In the case of coal firing many firemen are devoted to what is known as "spreading firing" or "spreading," as this method gives them the least trouble, but it should not be allowed owing to the fact that it is uneconomical and black-smoke-producing. If the practice of firing little and often is coupled with "spreading," and if due care is taken to admit the correct quantity of air, the production of black smoke is much reduced, but as this method means hard work it is not likely to receive favour at the hands of the ordinary still fireman.

The best method of firing is known as "coking firing," and it consists in shovelling the coal on to the dead plate and front ends of the firebars. As the fuel becomes incandescent it is pushed towards the back of the grate and more "green" coal supplied to the front. With this method, there is little if any black smoke, and there is a saving in coal consumption. The thickness of the fire should not be less than 5 to 6 inches, and shallow places must never be allowed to form. If they do an excess of air will pass through into the combustion chamber, and this will reduce the temperature of the hot gases, tend to retard perfect combustion, and raise the fuel consumption per ton of tar distilled. In theory, 12 lbs. of air are required for each 1 lb. of coal burned, but in practice it is necessary to supply 18 lbs. to 20 lbs. for this amount of coal. To obtain the proper quantity of air, careful attention must be paid to the manipulation of the flue dampers and the air grids on the fire doors, as well as to the thickness of the fire and the regular cleaning of the firebars.

In the case of gas firing one of the first things to be borne in mind is the risk of explosion on lighting up if a very simple precaution is not taken, namely, that of placing a few shovelfuls of burning coal or some lighted cotton waste on to the floor of the furnace before turning on the gas supply. Often a small fire is lighted on the firebars of the still furnace, using slack, and when well alight the gas is turned on. Occasionally small quantities of slack are spread over this fire, so that the firebars are kept covered to a depth of about 2 inches.

Some prefer not to use a small coal fire, as just described, and yet retain the type of furnace employed for coal firing, in case the gas fails. What is done in cases like these is to cover the firebars with firebricks, or to remove the bars and bearers and replace them with stopping. Of the two plans the latter is the better as it gives more furnace room and allows for a more satisfactory combustion. Whichever method is adopted the gas must be admitted gradually until the still fireman is satisfied that all the gas coming forward will be ignited.

As the gas-burners are supplied with air ports it is a much easier matter to regulate the air supply in order to maintain proper combustion than it is with a coal-fed fire. The proportion of air to gas is different to that necessary for the proper combustion of coal. Theoretically, for complete combustion it is about an equal volume, and in practice very little more than this is required. The best results are obtained with gas burners when the gas is supplied to them under a constant pressure, but to do this it is necessary to put in a gasholder.

DIRECTOR OF INDUSTRIES. Bengal

CHAPTER V

PLANT USED IN THE DISTILLATION OF TAR (*continued*)

Preheaters—corrosion of preheater coils—advantage of preheaters—condensing coils—corrosion of condensing coils—condenser coil tanks—steam coils—collecting and dividing boxes—foul gas mains—methods of dealing with foul gases—methods of running distillates to receivers—cocks—types of receivers—steam valves—pitch coolers—French weir cooler—pitch gutters—pitch bays—emergency pumps—plant for the dehydration of tar—plant for the continuous distillation of tar.

A PREHEATER (see Fig. 28) is very similar in shape to a tar still, the only difference being that the bottom is flat. It is constructed of wrought-iron or mild steel plates, and of a size to hold a little more than the charge for the still to which it is attached. As wear and tear are not very great, plates of moderate thickness are used in its construction; mild steel plates of $\frac{1}{4}$ inch or $\frac{5}{16}$ inch are quite thick enough. The mountings consist of: (*a*) A cast-iron charge pipe block or stool with a 6-inch or 8-inch hole, to which the charge pipe is connected; (*b*) a small cast-iron swan neck fitted on to a cast-iron stool, for connecting to the vapour pipe, which in its turn is fixed to a common main leading to a condensing worm. The swan neck may be 4 inches bore at the inlet, tapering to 2 inches at the outlet. In the writer's opinion 2-inch or $2\frac{1}{2}$-inch wrought-iron steam-pipe, extra thick quality, suitably bent and connected to a flange, serves this purpose quite as well. (*c*) A $1\frac{1}{2}$-inch cast-iron gland cock fitted near the top of the preheater, through which a dipping rod may be inserted in order that the workman can find out when the vessel is charged correctly; if desired, instead of a dipping tap a flange can be riveted on and fitted with a $1\frac{1}{4}$-inch plug, the plug being removed each time a dipping operation is to be carried out. (*d*) A wrought-iron screwed flange of 2-inch bore, to which is fitted a 2-inch wrought-iron overflow pipe. This pipe is connected to a common main leading to a special tar tank. The overflow outlet is placed in such a position that at the finish of a distilling operation a correct still charge of hot tar remains in the preheater. (*e*) A wrought-iron pipe of 3-inch bore, which is known as the discharge pipe, to which is connected a 3-inch cast-iron gland cock. This pipe is placed on the side of the preheater at the bottom. (*f*) A manhole of 18 inches by 12 inches with draw-up lid. (*g*) Two extra deep, screwed, wrought-iron flanges of 3-inch bore, one placed so that its centre is about 3 feet 6 inches from the bottom and on the same side as the discharge pipe stool,

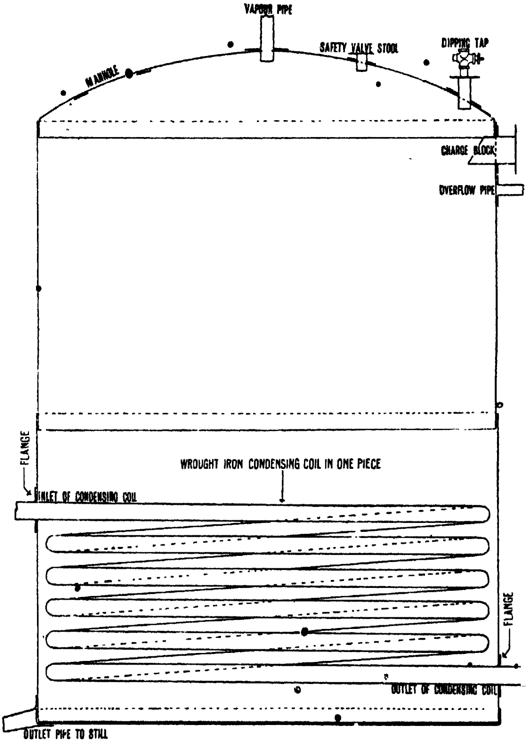

FIG. 28.—Diagrammatic representation of Preheater.

and the other on the opposite side as near the bottom as possible. These are for admittance and egress of a condenser coil, which is fixed inside the preheater. (*h*) A safety-valve or other suitable contrivance.

The condenser coil is made of 3-inch wrought-iron steam-pipe, but it should be of extra thick quality, viz., $\frac{5}{16}$ inch, in order to reduce the repair bill. The coil suffers severely from internal corrosion, especially the top lap; and in the writer's experience wrought-iron steam tube of ordinary thickness ($\frac{3}{16}$ inch) has corroded through on the top lap in less than six months, against 18 months if $\frac{5}{16}$-inch tube is used. The length of the coil may be approximately 160 feet, arranged in say 6 laps. Investigations made by the writer and others indicate that the corrosion of preheater coils is due chiefly to dissociated ammonium chloride and ammonium sulphide, the temperature at the top lap being particularly favourable to chemical action. The preheater is erected in an elevated position, so that the condensing coil may be attached to the swan neck of the still, and the hot tar be discharged into the still by gravity. It should be properly lagged with insulating material.

Several advantages are secured by the employment of preheaters, the chief of these being: (*a*) There is a saving of fuel owing to the fact that hot tar is charged into the still, the tar absorbing part of the heat from the distillates passing through the preheater coil which otherwise would be lost; (*b*) the time of the distilling operation is reduced, as: (1) some of the entangled ammonia water is driven off, (2) a portion of the crude naphtha is distilled off, and (3) less time is taken to bring the still "round" (*i.e.* commence the distillation), owing to the tar being hot when charged into the still; (*c*) more tar can be worked in a given period, because it is not necessary for the tar still to cool down to any great extent before charging again, as would be the case if cold tar had to be dealt with.

Connected to the outlet of the preheater coil, or, if a preheater is not used, direct to the swan neck, is the inlet end of the condensing coil proper. This piece of apparatus consists of laps of pipe, each lap being circular, square, or rectangular in plan, the circular type being the most general. A coil can be made of cast-iron or wrought-iron; the latter metal is preferable, as the thickness of a cast-iron coil hinders somewhat the cooling or warming of the distillates, as the case may require. Another disadvantage in connection with cast-iron coils is the presence of a large number of flange joints, which introduces frequent trouble in the nature of leaking. Wrought-iron coils are manufactured of considerable length in one piece, and a coil of this kind will do away with the chances of the distillates leaking out, or the water surrounding the coil leaking in, as is so liable to occur in the case of flange joints. The bore of condenser coils may vary between 2 inches and 4 inches, and the length between 130 feet and 300 feet, according to the size of the still. A distance of not less than $3\frac{1}{2}$ inches should be allowed between each lap. As an example, for a 20-ton still provided with a preheater about 130 feet of 3-inch wrought-iron pipe is sufficient. In order that the coil may be cleaned, it is advisable to arrange for a ¾-inch steam inlet, so that steam can be blown in after each operation. This provision will also assist in loosening a stoppage, should this occur. The steam inlet may be placed at the top of the coil before it enters the condenser tank.

The condenser coil is corroded from the top downwards, but not to such a great extent as the coil in the preheater. The corrosion also takes place from the outside, as well as the inside, especially at the top lap at the "wind and water" line. On an average the top lap, if made of wrought-iron tube of $\frac{3}{16}$ inch in thickness, will last three years. It is possible to cut out the top lap when it is corroded through and join on a new lap; but if this is done, care must be taken to make a thoroughly good joint. The writer can recommend wrought-iron tube of $\frac{5}{16}$-inch thickness for the construction of a condenser coil.

The condenser tank will vary in shape and size according to the type and dimensions of the coil it is intended to put into it, or whether the tank is to contain more than one coil. Generally the shape is cylindrical and of a size to contain one coil. Wrought-iron plate or mild steel of ¼-inch or ⅜-inch thickness or cast-iron sections may be used to build the tank. In arranging for the size, due allowance should be made for water space between the outer edge of the coil and the tank side; 6 inches is a good margin. The bottom lap of the coil should not rest on the tank, but should have a clearance of between 4 inches and 6 inches. A 1½ inch drain cock should be placed in the centre of the bottom of the tank, by which to run off the water in case the tank or coil requires repairing, or when the tank and outside of the coil require cleaning. A hole must be cut in the tank bottom, through which to put the coil end. A good cold-water supply should be run to the tank, and the inlet pipe must extend to within 3 inches from the bottom of the tank. About 2 inches from the top of the tank the water overflow pipe is inserted; it should be so arranged that practically all of the top lap of the condensing coil is covered with water. The water inlet and overflow pipes may be of 1½-inch or 2-inch internal bore. It is necessary to place a perforated steam coil of one turn on the bottom of the tank, and a 1-inch steam-pipe is large enough. This is used to assist in raising the temperature of the condensing water at one period of the distilling operation, and also to aid in the removal of an obstruction of, say, creosote salts in the coil, should this occur.

The worm or coil end, after it leaves the condenser tank, is shaped in the form of a U in order to form a seal. One leg of the seal is connected to a small cast-iron tank known as a receiving or collecting box (see Fig. 29). This box should be covered with a cast-iron lid and water-sealed. In the lid a perfectly fitting sliding door is fitted (see Fig. 29), in order that the workman may inspect the distillates as they flow from the worm end, and also collect samples of them for testing purposes. The bearing parts of the slide and its frame should be kept thoroughly greased.

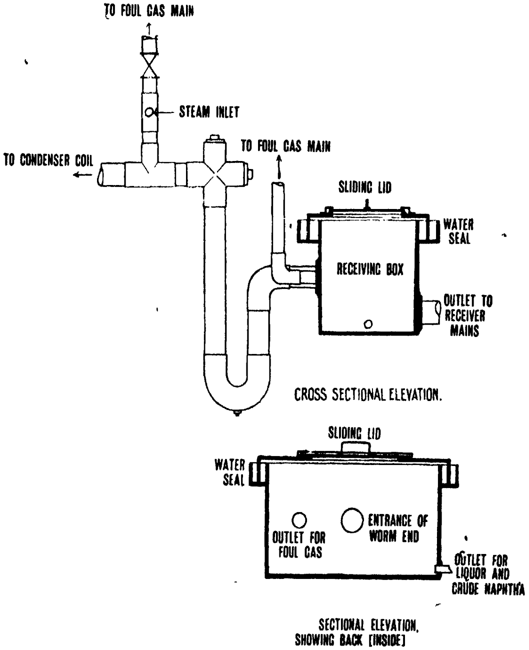

FIG. 29.—Receiving Box and Connections.

Two outlets are made in the sides of the box, through which the distillates are run, and one outlet is provided for making a connection with the foul gas main. One of the distillate outlets is connected up to a piece of apparatus known as a dividing-box, in which ammonia water is separated from crude naphtha, and the other to a pipe which is coupled up to the several receiver mains. Collecting boxes vary a little in size and shape, but for most purposes 2 feet 6 inches by 1 foot 6 inches by 1 foot 6 inches deep is quite large enough.

The dividing box is made of cast-iron, is cylindrical in shape, about 1 foot 9 inches in depth and 1 foot 3 inches in diameter. It is provided with a water-sealed cast-iron lid, in which is made a 6-inch inspection hole, covered with a lid, the bearing parts of which must be kept greased. There are two outlets, one which leads to a small piece of apparatus known as a water box, really a water-sealed inspection chamber, on the ammonia water main, and the other is connected up to the main which leads to the crude naphtha receiver. Each outlet is made of a sufficient size to insert a 1-inch wrought-iron pipe at about 4 inches from the top of the box. The centres of the two holes are on the same level, and the outlet pipe which conducts the crude naphtha away just enters the cylinder, and on to it is fitted a movable elbow to regulate the flow somewhat, while that which deals with the ammonia water bends down inside the box and reaches to within 1½ inches of the bottom (see Fig. 30). The inlet pipe from the collecting box is of 1-inch wrought-iron pipe, and is inserted in the cover of the dividing box. A wrought-iron connector should be placed in this pipe in order to facilitate removal if it becomes necessary to uncover the box.

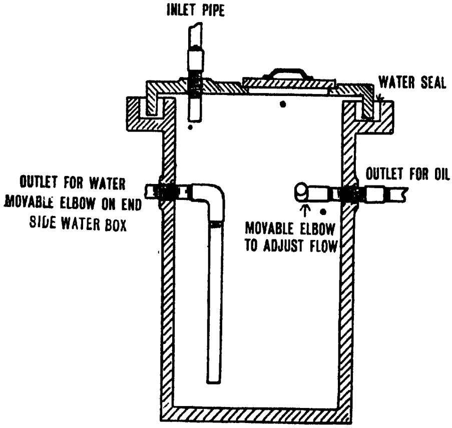

FIG. 30.—Dividing Box.

The water box or inspection chamber (see Fig. 31) is a small cast-iron vessel about 8 inches by 8 inches by 8 inches deep, internal dimensions. It is provided with a cast-iron lid, water-sealed, and one 1-inch inlet hole at the side near the top, and another 1-inch outlet hole at the bottom on the opposite side. Through the inlet hole is inserted the ammonia water pipe coming from the dividing box, and on to the end of the pipe is fitted a movable elbow to enable the workman to regulate the flow of the liquor. To the outlet is fitted a 1-inch wrought-iron pipe, which leads to the common liquor main running to the ammonia water receiver.

In order to comply with the Alkali Act, it is necessary to prevent the discharge into the atmosphere of all offensive or noxious gases, such as are given off from tar distillates, especially at the worm end, and to render these gases innocuous in some suitable manner. The plant used in tar works for this purpose varies somewhat according to the ideas of the management. In all cases it is necessary to provide foul-gas mains, to conduct away the gases and fumes from (*a*) the worm ends and collecting boxes; (*b*) the receivers; and (*c*) the pitch coolers. Lengths of $2\frac{1}{2}$-inch or 3-inch wrought-iron pipe are fitted in close proximity to the various pieces of apparatus just mentioned, forming common mains, and the worm ends, collecting boxes, etc., are connected to these mains by means of T-pieces. One end of the common main is connected up to a steam-pipe, so that steam may be blown through frequently for cleansing purposes, and the other end to an exhaust pump or

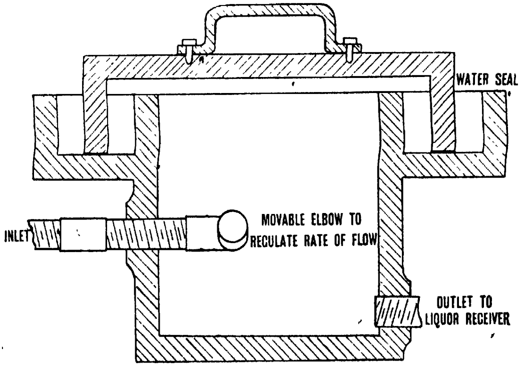

FIG. 31.—Water Box.

steam ejector, either of which draws away the foul gases, and delivers them to the boiler furnace to be burned, or to a special apparatus for treatment with a view to recovering sulphur, etc. In all cases in which it is intended to burn the gases it is advisable to draw them through a water seal of a design somewhat similar to a wash-bottle (see Fig. 32). This precaution will minimise the risk of a "flash back" taking place throughout the whole system. It must be remembered, however, that if the ejector is not carefully attended to, the risk of a "flash back" taking place and producing an explosion in the seal pot is great. The seal pot should be kept filled with water to three parts of its depth, and in the cover a hinged lid is fitted, and always kept unfastened; the bearing parts being well greased with heavy lubricating oil, to make a more or less tight joint. The writer's experience of this method of dealing with foul gases has been a satisfactory one. A good plan, in order to see whether the exhausting apparatus is working efficiently, is to fit one or two manometers into the main in suitable positions.

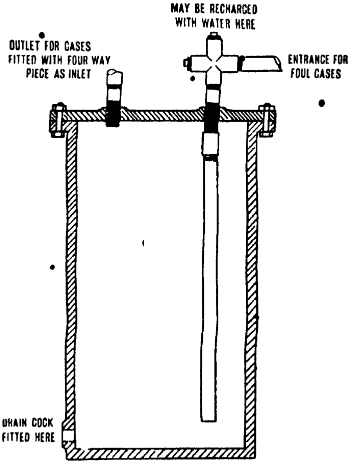
MAY BE RECHARGED WITH WATER HERE
OUTLET FOR GASES FITTED WITH FOUR WAY PIECE AS INLET
ENTRANCE FOR FOUL GASES
DRAIN COCK FITTED HERE

FIG. 32.—Seal Pot for Foul Gas Main.

Owing to the corrosive action of the foul gases, the wear and tear on the cones of the ejector is very considerable. The writer strongly recommends the use of malleable iron cones in the place of gun-metal, which is often used. The figures given in Table XIV, the average of several experiments, will support this recommendation.

TABLE XIV

	Gun-metal.	Malleable iron.
Diverging cones lasted .	6 months	13 months
Converging cones lasted .	8 ,,	24

Some distillers prefer to deal with the foul gases by passing them through an oxide purifier, more of less similar to a gasworks plant but on a smaller scale. The oxide is revivified as usual, and eventually sold for the manufacture of sulphuric acid.

A method of purifying foul gases by scrubbing with water and then passing through absorbing towers containing hydrate of iron in suspension in water was devised by J. Craven and W. H. Coleman, and published by them in the *Journal of the Society of Chemical Industry*, vol. xx. p. 200. This method is certainly a very safe one, and by it any ammonia, light hydrocarbons, and sulphur in the gases are recovered.

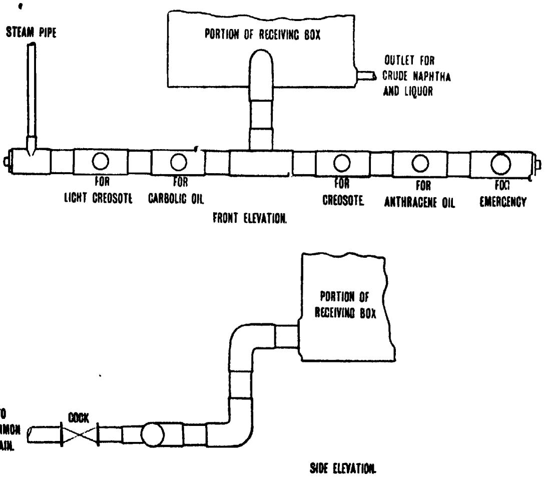

FIG. 33.—One Method of connecting Common Mains to Receiving Box.

The various distillates from a battery of tar stills are led from the collecting or separating boxes to common mains, the latter being connected up to the receivers. Each of these common mains should be provided with a 1-inch steam inlet at one end for the purpose of introducing steam for cleaning after each operation, and to assist in removing obstructions should these occur. Endeavour should be made to keep the cocks which control the flow of the various distillates from the collecting box to the common mains as near one another as possible, and they should be suitably marked; it saves time and prevents mistakes. A method of doing this is shown in Fig. 33.

The internal diameter of the common mains will vary according to the number of stills feeding them at one time; from 2 inches to 3 inches is generally found suitable. Connections between the collecting boxes and common mains may be of 1½ inches to 2 inches internal diameter.

Good cocks should be put into all these mains, and also all the pumping mains about a tar distillery. Those made of cast-iron are the best to use, and the most satisfactory type is that known as the Butterfield cock. Generally cast-iron gland cocks are employed, but unless the glands and packing are carefully and periodically attended to, leakage of a more or less serious character will take place. A cock of the Butterfield type (see Fig. 17), if properly put in, requires very little attention, and it will not leak even in a main through which hot creosote oil and steam are continually passing. The writer has in his experience known gland cocks to require attention every two or three days, and the packing seeing to about every month, whereas a Butterfield cock put in the same main required no attention or packing for a period of one year and nine months. No leaking took place from the latter cock, but from the former serious leaking often occurred.

It is of course necessary to provide a receiving tank for each fraction taken off the tar. The number will, therefore, vary according to the manner in which the tar is worked up, or the nature of the tar distilled. Generally there are seven receivers provided, one for overflow tar and one for each of the following distillates: ammoniacal liquor, crude naphtha, light oil, light creosote, heavy creosote, and anthracene oil. Flat-ended boiler tanks (*i.e.* old steam boilers from which the tubes have been drawn and the ends blanked) make very suitable receivers. They must, of course, be in first-class condition, free from all poor seams or thin plates. It is not possible to give any definite figure as regards size, as this must necessarily vary according to the quantity of tar worked per day and the amount of storage room. For a works distilling say 100 tons of tar per day, receivers of an average capacity of 8000 gallons will be found quite suitable. Some works use specially made tanks of a size just sufficient to hold a little more than one of the various fractions worked off a single charge of tar. This, it is contended, enables the manager and workmen to check in a more efficient manner the yield of the several fractions from the tar.

All but the crude naphtha and ammonia receiver should be provided with a closed steam coil. One turn of 1-inch steam-pipe covering the whole bottom of the receiver will be found sufficient, provided an efficient steam trap is connected with the exhaust end. Each receiver must have a manhole, which, with all the other openings, should be properly covered, to prevent loss by evaporation in the case of the light distillates, and in all cases the escape of foul gases. It is desired by some to connect all the receivers to a foul gas main, but this is not absolutely necessary if all the openings are kept well covered. The contents of the receivers are removed to storage tanks, or washing tanks, by: (*a*) pumps, or (*b*) compressed air. In the latter case it is necessary to supply an air inlet, and also an exit pipe, which must reach to within about half an inch of the bottom of the lowest portion of the receiver. It is much better to put in a small dish plate at the bottom, as shown in Fig. 34. Arrangements must be made to seal the receiver completely; if this is not done removal by compressed air becomes an impossibility. For the compressed air pipe, 1-inch steam tube is quite suitable, and for the delivery or exit pipe, 2-inch steam tube is the best size to employ.

If it is desired to remove the receiver contents by the aid of a pump, then a 2-inch suction pipe should be put in. This can be arranged so that it will reach to the bottom, or be lifted to any point in the receiver. It is a general plan to connect the suction pipe of all the receivers to a common pumping main and pump, cleaning the two latter by blowing steam through after the pumping operation is finished. Although not absolutely necessary, it is a good plan to connect each receiver to a special emergency main and pump; it sometimes comes in handy when working difficulties arise.

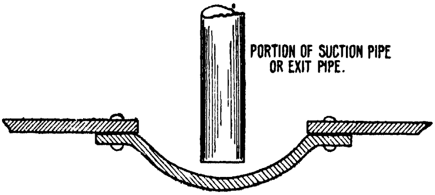

FIG. 34.—Dish Plate at Bottom of Receiver.

It will not be out of place here to consider briefly the subject of steam valves, in particular those used round about the tar stills, condensers, collecting boxes, receivers, foul gas mains, etc. The valve in general use is made of gun-metal, and is of course quite suitable for all positions where sulphuretted hydrogen, ammonium sulphide, or ammonia vapours are not in evidence. If these vapours come in contact with the gun-metal shell of the valve, very rapid corrosion will take place, and a fracture eventually occurs. Cast-iron or cast-steel stop valves do not corrode anything like so rapidly, and are, therefore, much more suitable. It is advisable to lag the valves, and also all the steam-pipes, with a non-conducting composition.

Owing to the high temperature at which it is necessary to run the pitch from the still, it is absolutely essential to keep it out of contact with the atmosphere and to cool it in some manner or other before running it on to the pitch bay. If this is not done, there is a great risk of spontaneous combustion of the hot vapours taking place, and a firing of the pitch; and even if the temperature of the pitch is too low for this to occur, acrid vapours are given off in great volumes, which will cause a nuisance in the neighbourhood of the distillery. In order to meet these requirements coolers made of wrought-iron or mild steel, cylindrical or square in shape, are most frequently employed. The former shape is, of course, the most suitable, as it withstands much better the great strain brought about by running the very hot pitch into the cool receiver. A cooler is provided with a manhole of not less than 18 inches by 12 inches or 18 inches in diameter; a manlid stool, and cast-iron lid; an inlet pipe stool, to couple up to a 4-inch or 6-inch pipe, according to the diameter of the still tail pipe; an outlet valve of the "treacle" or gate type of about 6 inches, or of the lever plug type and not less than 4 inches; and a 2-inch outlet for connecting up to a foul gas main. The manlid is left loose in order to act as a kind of safety-valve, and it may be sealed by embedding into a lime-putty, or covering the bearing surfaces with a layer of thick grease. Old cylindrical steam boilers, from which the tubes have been drawn, and the ends blanked, answer admirably as pitch coolers, provided the plates are thick enough, and the riveted seams are in good condition. The plates of the cylinder should be of not less than ⅜ inch and the ends ½ inch in thickness, or better still a thickness of ½ inch throughout. Each cooler should be raised a little above the ground level, say 1 foot 6 inches to 2 feet, to allow inspection for leakage to be made, and also to enable the air to circulate all round it. It may be supported on brick or concrete cradles. A fall towards the outlet of about ½ inch to the foot should be allowed.

Pitch coolers are sometimes built in the form of brick chambers, but as it is not a general practice this form will not be considered.

In a works dealing with large quantities of pitch, a pitch cooler built on the plan known as the "French weir" will give excellent results. There are two chambers in this cooler (see Fig. 35), that marked R in the figure being the one into which the hot pitch is run from the still and in which part cooling takes place. In the other chamber, marked C, the cooling is completed. When a fresh charge of pitch is run into R it pushes the cooled pitch contained in C through the outlet O into the pitch bay.

In order to convey the pitch from the coolers to suitable positions in the pitch bay, where the final cooling and solidifying prior to "getting" or digging takes place, a gutter is often built under the outlets of the coolers. The gutter should be provided with several outlets closed with gate or sluice valves, in order to direct the pitch into one portion of the bay to cool and solidify, while "getting" is going on in another portion. As regards the arrangement of this gutter, this will of course have to be made to suit the position of the coolers, and varies in different works. Concrete may be used to construct the gutter, the surface being rendered with a mixture of cement and sand, but it is far better to line the gutter throughout with brindled tiles or smooth bricks set in cement, as by doing this the removal of cold pitch during cleaning is facilitated. A depth of 2 feet 6 inches to 3 feet is ample, and it should be level from one end to the other. The sides of the gutter may be 14 inches or 18 inches thick, not less than the former. It should be so arranged that the gate valves can be operated by the workman in safety from a position opposite to that which the pitch runs into the bay. A method designed by the writer is shown diagrammatically in Fig. 36. The gate may be raised and lowered by means of a rack and pinion or worm and wheel gear. In some works gutters are not used, but one is cut in the cold pitch on the bay in any desired direction. This is not a good plan.

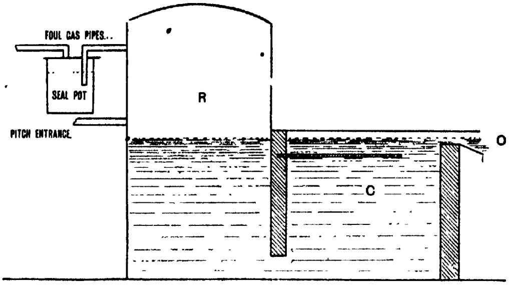

FIG. 35.—French Weir for Pitch-cooling.

The pitch bay is situated in close proximity to the coolers at a lower level to them and the gutter. It should not be too deep, but of wide area, the dimensions varying according to local conditions and the amount of tar worked up. A depth of 2 feet 6 inches below the gutter outlets is a good average; pitch of a greater thickness than 2 feet is more difficult and expensive to "get." The floor and sides of the bay are concrete or brick lined. As regards the floor, a brick lining placed on a concrete bed proves the most suitable. The bricks should be smooth faced and of the best Staffordshire blue brick type. They should be set closely in good cement, and the whole floor must be level. It is advisable to divide the bay into several sections, say three or four, by building 14-inch walls across it.

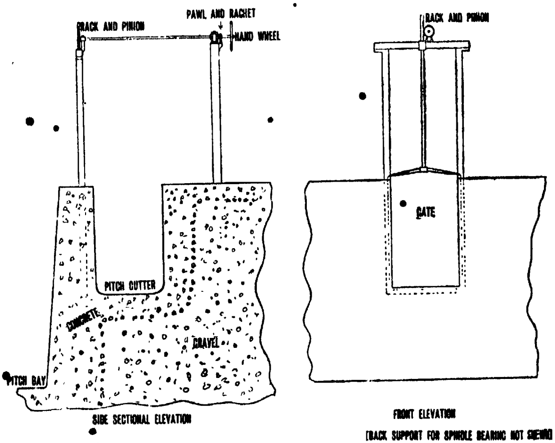

Fig. 36.—Pitch Gutter Outlet showing Gate Valve.

If it is wished to avoid the expense of doing this, temporary partitions can be put up with wooden planks and loose pitch, or by leaving a wall of hard pitch from a previous "getting," but these methods are of doubtful value, as the partitions sometimes give way at most inconvenient times. The object of dividing the bay into sections is to allow one batch of pitch to cool while another is in the process of "getting."

It is as well to endeavour to arrange for a private railway siding to run alongside the pitch bay, and it is of great advantage if that siding is at such a level that the top of the railway trucks are practically in line with the floor of the bay. This will enable the pitchmen to wheelbarrow the pitch direct into the trucks and save the cost of a crane, skips, and a crane driver.

There are times when a tar still springs a leak, and it then becomes necessary to empty that still with all speed. In order to do this a permanent 3-inch wrought-iron main should be run along the back of the battery of stills, and a branch from this

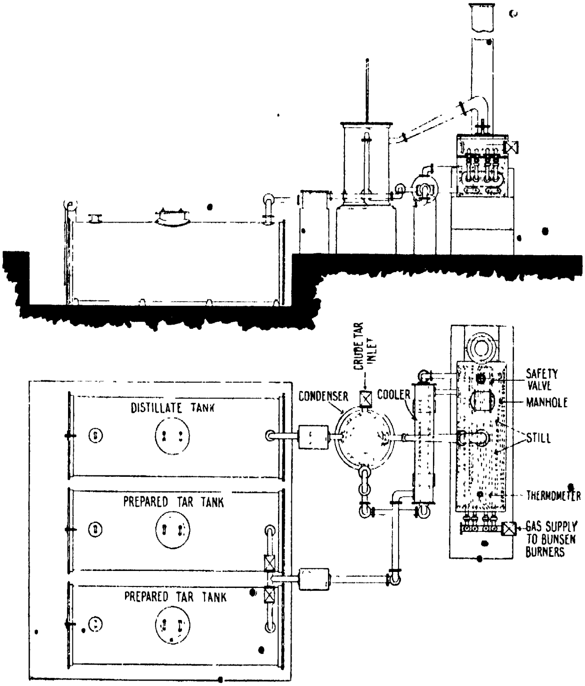

FIG. 37.—Diagrammatic Illustration of Hird's Tar-dehydrating Plant.

main fixed in a suitable position, so that after the connection between the tail or run-off pipe of the still and the cooler is taken apart, immediate connection with this branch can be made. One end of the main should be closed with a plug, and the other end connected to a special pump kept especially for emergencies of this nature. The same pump can be used, if desired, as an auxiliary to the creosote pumps, but should always be so connected that it can be put into use on the tar emergency main immediately it is required. If the tar well is below ground, a pump is not absolutely necessary, as, the still being above ground level, the tar would run by force of gravitation into the emergency main and thence to the well. However, speed is a matter of importance at times, and then a connection to a pump would prove of benefit, even when the tar well is below ground.

Plants for the dehydration of tar have of late come much to the fore, and a brief description of Hird's dehydrating plant will, no doubt, prove useful. One capable of dealing with half a ton of tar per hour consists of the following pieces: one still, a cooler, one condenser coil and tank, one distillate tank, and two prepared tar tanks, with the necessary pipes and connections (see Fig. 37).

The still, which is constructed of mild steel, has fitted down the centre a longitudinal baffle, the function of which is to direct the tar first down the length of one side of the still and then up the other side. Four tubes, which are expanded into the end plates, run the whole length of the still, for the purpose of carrying the hot gases with which to heat the tar. The far ends of the tubes open into the base of a waste gas stack, and the near ends form the entry for four bunsen burners. These burners are connected to a common gas main. To the still is fitted a swan neck and safety-valve, and it is also provided with an oval manhole with a draw-up manlid, and a thermometer for regulating the temperatures.

Between the condenser and the still is fitted a cooler, or rather a heat interchanger, which consists of two steel tubes, one running through the other, the outer tube forming a jacket round the inner. Tar from the condenser tank travels through the inner tube on its way to the still, while the hot prepared tar flows through the outer tube or jacket on its way to the receiver.

The condenser tank is cylindrical, and is provided with an inlet and outlet for cold tar, which is used for cooling. In this tank is placed a cast-iron condenser coil, the top of which is connected to the vapour pipe leading from the still, while the bottom is joined to an inspection box, which in its turn is connected to the distillate receiver.

Set in a well, and on cradles, are the distillate receiver and two prepared tar receivers. These vessels are cylindrical in shape, and they are provided with a circular manhole, an inspection hole, a wire and weight gauge, and the necessary inlets from the condenser coil and tar cooler. Cocks are fitted near the inlets on the tar receivers, so that one receiver can be used at a time.

The continuous distillation of tar down to pitch is a process much older than that of continuous dehydration; in fact the latter is simply an offshoot of the former.

One of the earliest systems of continuous distillation which received any serious consideration is Lennard's (1888). The plant with which to carry out this system was designed on the cascade principle, was rather complicated, and was an expensive one to erect. More recently the Hird and Wilton systems have appeared, and the results obtained by them have proved very satisfactory.

Hird's patent system (Figs. 38, 39, 40, 41, and 42) requires

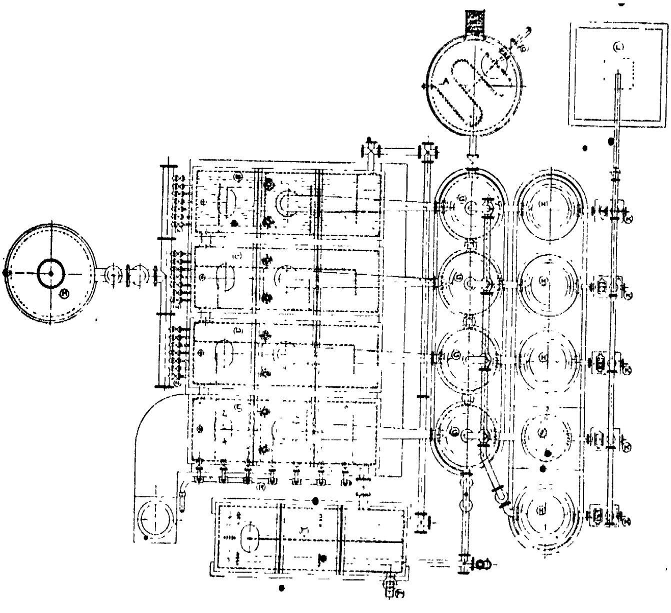

FIG. 38.—Plan of Hird's Continuous Tar Distillation Plant.

the following pieces of apparatus: A feed or regulating tank, four stills (Nos. 1, 2, 3, and 4), a pitch cooler, four combined heater-coolers, five water condensers of the coil type, five sight boxes, an oxide purifier, and, if the plant be heated by gas or producer gas, three sets of gas-burners are necessary.

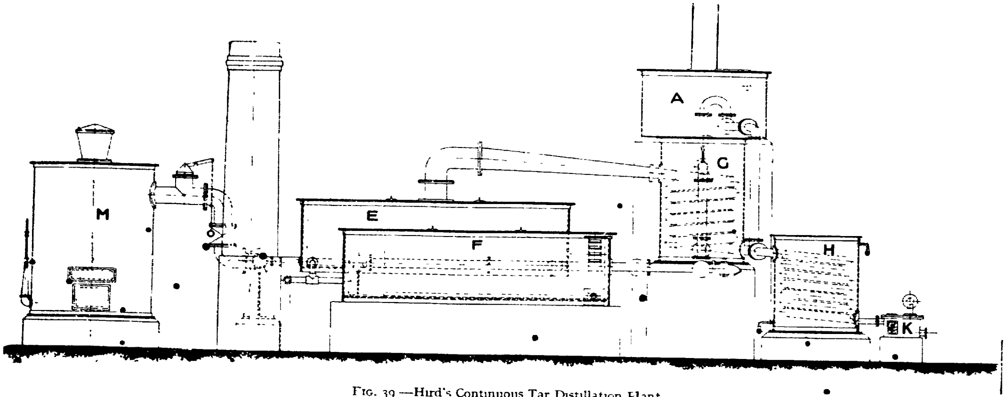

FIG. 39—Hird's Continuous Tar Distillation Plant.
A, Tar Regulating Tank. E, No. 4 Still. F, Pitch Cooler G, Combined Heater and Cooler. H, Coil Condenser. K, Sight Box.
M, Gas Producer.

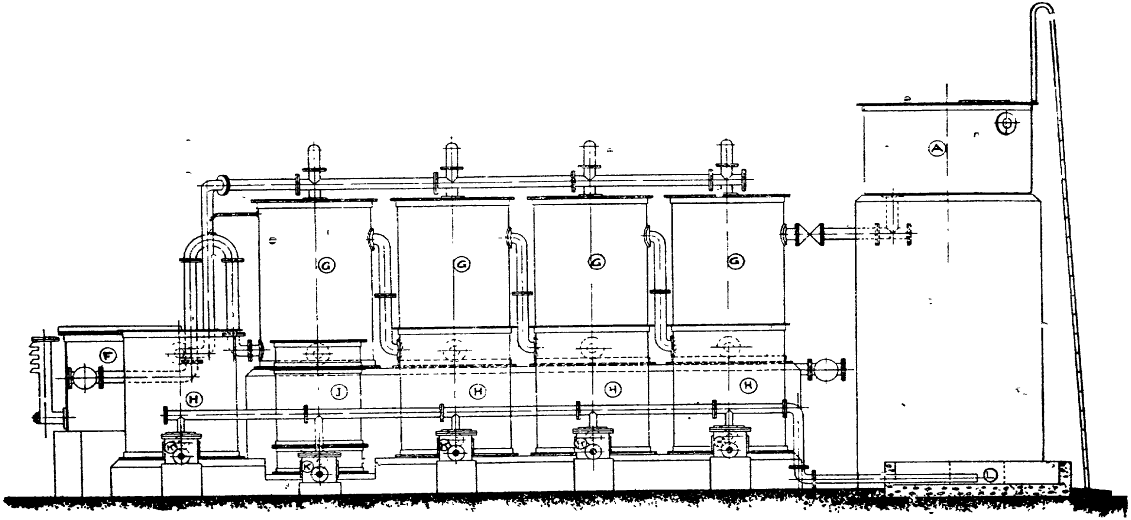

FIG. 40.—Hird's Continuous Tar Distillation Plant.

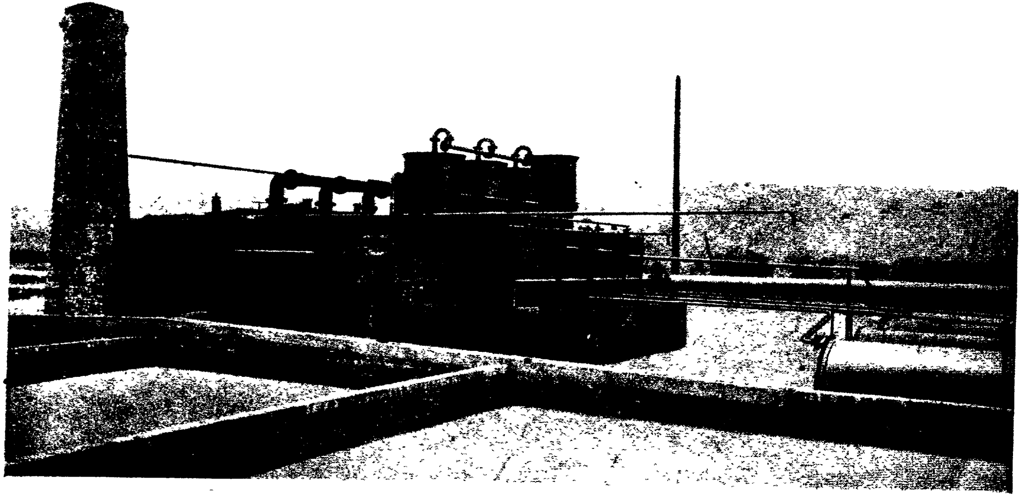

FIG. 41.—Hird's Continuous Tar Distillation Plant.

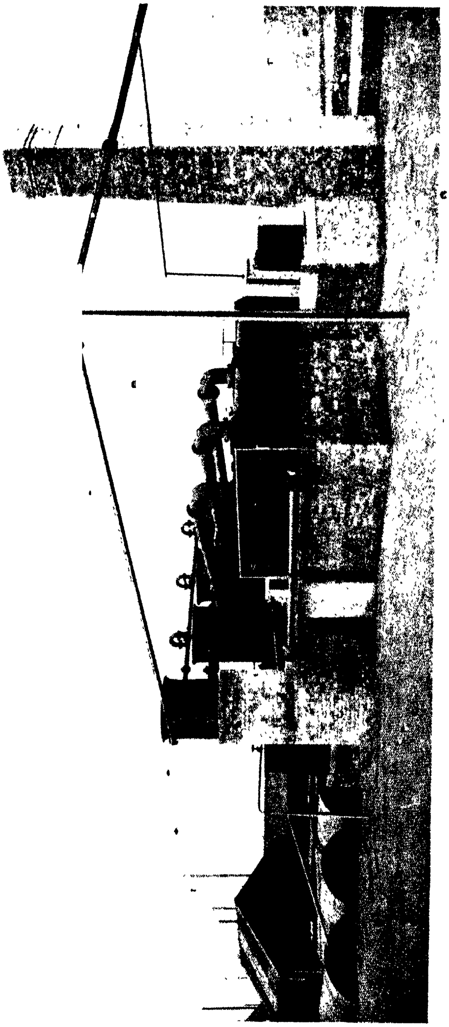

Fig. 42.—Hird's Continuous Tar Distillation Plant.

The feed or regulating tank is provided with a float valve in order to maintain a constant head of tar in the stills.

All the four stills are built of cast-iron, the separate parts having flanges cast on them so that they can be bolted together on the outer side of the still. As this type of still is not subjected to such drastic temperature treatment as a pot still, the mode of heating being internal, this method of construction is permissible, and from the point of view of corrosion is one which offers an advantage. Cast-iron is not attacked by dissociated ammonium chloride at anything like the rate that wrought-iron or mild steel is. Each still is provided with a manhole, a swan neck and vapour pipe, a thermometer, and a safety-valve. Internally there are four baffle plates fitted across the width of the still in such a manner as to cause the tar to flow in a circuitous manner from inlet to outlet. The arrangement of the baffle plates in Nos. 2 and 3 stills is rather different from that in Nos. 1 and 4 stills, as will be seen on reference to the diagram (Fig. 38).

Nos. 1, 2, and 3 stills are provided with longitudinal heating tubes, all of which are expanded into the end plates of the still, and for each of these tubes a bunsen burner is supplied. No. 4 still is supplied with seven lengths of open steam-pipe, all of which enter the side of the still. No. 1 still has an inlet for the heated crude tar and an outlet for the partially distilled tar, No. 2 still is connected immediately to the outlet of No. 1 and the inlet of No. 3, and No. 3 still to the outlet of No. 2 and the inlet of No. 4. The last still, No. 4, is provided with a pitch cooler outlet which is connected to the pitch cooler.

The pitch cooler is provided with a manhole and fitted inside with a baffle plate so arranged that the pitch will flow up one side of the cooler and down the other before it leaves for the pitch bay. A cast-iron pipe is fitted inside the cooler and runs up one side and down the other. This pipe conducts the hot tar from the heater-coolers to the stills. A weir valve is fitted to the outlet of the pitch cooler so that any seal of tar in the still can be obtained as desired, this being an advantage in working different classes of tar.

The heater-coolers consist of wrought-iron tanks, each provided with an inlet near the top and an outlet near the bottom through which the crude tar is conducted on its way to the pitch cooler and the stills. Each heater-cooler is fitted inside with a cast-iron coil connected at the top to the vapour pipe and at the bottom to the top of the coil of the water condenser. As distillation takes place from the heater-coolers, each cover is fitted with an outlet connected to a common main which conducts vapours to a water condenser.

The five water condensers are constructed in wrought-iron and fitted inside with a cast-iron coil. The top of the coil is connected with the bottom of the heater-cooler coil, and the bottom of the coil to the sight box. Each condenser is fitted with inlet and outlet for water supply for the purpose of cooling the distillates.

Connected to the coils of the water condensers are sight boxes. These are provided inside with a seal to prevent foul gases from getting into the atmosphere. Each sight box is also provided with an outlet for the condensed distillates and another for the foul gas.

The foul gas main is connected to an oxide purifier, which consists of a brickwork sump filled with lime and oxide of iron.

The plant can be heated by any known means. The methods which give the best results are heating by gas, using bunsen burners and allowing the flame to play direct into the heating tubes, and by a coke-breeze furnace. In the latter case the heating tubes are connected to the furnace by means of silica tubes.

It takes about eight hours to get the plant into working order, after which only a very small amount of supervision is required. In this plant tar can be fractionated into ammoniacal liquor, crude naphtha, light oil, creosote oil, anthracene oil, and pitch, and the distillates leave the plant uniform in quality.

CHAPTER VI

DISTILLATION OF COAL TAR

Charging preheater and still—commencing the distillation—crude naphtha and ammonia water stage—light oil stage—carbolic oil stage—creosote stage—anthracene oil or "green oil" stage—introduction of steam—Wells' oil—method of testing used by stillmen—examination of safety-valves, etc.—running off pitch—recharging still—discharging pitch and preparation of bay—still cleaning—dehydrated tar—tar for road treatment—remarks on Road Board specifications—tar for roofing felt—continuous dehydration of tar—continuous tar distillation—tar distillation balance-sheet—working costs.

THE object of distilling coal tar is to increase its usefulness, and, therefore, its commercial value. Broadly considered, the process of distillation is the same in all works. It differs only in certain details, such as (*a*) the method of testing for the "cut" or "change-over point" for each fraction, (*b*) the number of fractions a certain tar will yield, or it is desired to collect, (*c*) the wish to manufacture special products from the fractions, (*d*) the quality of pitch required, and (*e*) whether it is required to make special preparations from partly distilled tar, and so on.

By far the largest portion of the tar which passes through a tar distillery is worked for benzols, naphthas, creosotes, naphthalene, anthracene, carbolic and cresylic acids, pyridine and pitch, and the distilling of a charge of tar for the various fractions from which these products are obtained, and for pitch, will receive attention before dealing with special preparations. It will be assumed that a preheater is connected to the tar still, and that both are empty.

A charge of tar is pumped into the preheater from the storage tank or well. It is desirable to work well settled tar, as some of the entangled ammonia water will have separated to the top, and in consequence less time will be occupied in distilling off this material. While charging the preheater, the manlid of the still should be placed into position, the joint being made of lime putty: a mixture of slaked lime and water of the consistence of butter. The condensing worms, mains to the receivers, and safety devices should be inspected to see if clear of obstruction, *i.e.* not choked up with naphthalene or anthracene salts. A 15- to 20-ton preheater may be charged through a 6-inch main in between 30 and 45 minutes.

The preheater having been properly charged, the supply is cut off, and the tar turned into the still. As soon as the preheater is empty, *the discharge cock is shut off*, and a fire or the producer gas ignited. A further charge of tar is pumped into the preheater at the same time by the stillman's mate. The heating up of the tar may be pushed until the swan neck becomes hot, but immediately that sign becomes evident, considerable care must be exercised in order to avoid "priming" or boiling over of the tar. At that point, then, the fire is slackened a little, and the worm-end watched for the first drops of the distillate. The distillation is now proceeded with, with caution, and it may become necessary to slacken the fire a little more at this stage. Sufficient heat must, of course, be supplied to keep the distillate flowing gently from the worm-end into the collecting box. Should "priming" unfortunately occur, damping the fire, or shutting off the gas, and playing or pouring cold water on the still top will soon stop it. It is not a bad plan to run a 1-inch emergency water main across the battery of stills, and place in it several cocks and connect these to short lengths of hose. The tar which comes over during "priming" should be turned into the overflow tar receiver, the openings from the collecting box to the dividing box being promptly shut.

This portion of the distilling operation is known as the crude naphtha stage, and the fraction consists of ammonia water and crude naphtha. During the whole time the fraction is passing the water in the condenser tank must be kept running, and the supply should be cold. The distillate drops from the worm-end into the collecting box and then passes into the divider, where the ammonia water sinks to the bottom, and is removed by the water pipe to the inspection box, then via the liquor main to the receiver. The crude naphtha flows through the outlet near the top of the divider into the main, which conducts it to the receiving tank. For a while the amount of water in the distillate exceeds that of oil, but as time goes on the amount of the former decreases—the latter, of course, increasing. At this stage the temperature may be increased a little, but it is yet necessary to continue careful firing. The flow of the liquor and naphtha into the receiver mains is regulated by raising or lowering the elbows, the one inside the inspection box and the other inside the divider, as explained on pages 53 and 54 respectively. As the amount of water in the distillate decreases, so *with care* may the temperature be raised, but not unduly rapidly. Towards the finish of this fraction the small quantity of water still coming over will change in colour from a greenish yellow to a blood red. From now the stillman should collect occasional samples at the worm-end, allow the oil to separate, and take its specific gravity. When this reaches a figure prearranged by the works manager, the outlet to the divider is closed, and the cock on the light oil receiver main opened. This point is known in tar works terminology as the "change over" "cut," or "turn over," point. The specific gravity at the "turn over" point may vary between 0.950 and 0.965. Some stillmen "cut" the distillate when water ceases to come, but this method often results in a crude naphtha containing rather more heavy material than is desirable. The length of time required to work off this distillate will vary according to the state of the tar and the volume of the charge. With normal tar and a 15- to 20-ton charge, 6 to 12 hours may be taken as average times, and with reference to the yield of the distillate this may vary between 3 and 6½ gallons per ton of tar. During the working off of this fraction the pull on the foul gas mains should be slight, otherwise there will be a loss of light products if a recovery plant is not attached to the mains.

The strength of the ammonia water from the fraction is generally between 2 and 3½ per cent. of total NH_3, and this product is worked up at the tar distillery, or else sold to a firm of ammonia distillers. In order to avoid loss of ammonia, the receiver should be kept well sealed, and the liquor removed and dealt with as quickly as possible. Crude naphtha varies somewhat as regards specific gravity, but it usually ranges between 0.905 and 0.920. From it are obtained chiefly benzols and a little light naphtha. Full details on the working up of this material are given in chapters ix, x, xi.

Soon after the "change over" to the light oil fraction, the distillate will begin to run from the worm-end in a moderately thick stream, and practically free from water. The temperature is gradually increased, in order to keep the distillate running at an even rate. At times, when partly through this fraction, some water comes over with the oil. It is not usually necessary, however, to slacken the firing, and the beginner should not be alarmed if this occurs. As the process continues, the amount of naphthalene salts in the distillate increases, and it is necessary to keep this material from crystallising out and choking up the condensing coil. To avoid this, the flow of water through the condensing tank is stopped very shortly after the "cut" is made. The water in the tank then becomes gradually hot by absorbing heat from the distillate as it passes through the worm. Should the tar contain a large quantity of naphthalene "salts," making this fraction extremely "salty," it is advisable to bring the temperature of the water up more rapidly by introducing a little open steam into the tank. Generally the water is allowed to get hot when the specific gravity of the distillate stands at between 0.970 and 0.990 at 60° Fahr. The "change over" point from light oil to light creosote varies according to the nature of the tar, or if it is desired to make a distillate for a special purpose. On this account the stillman may "cut" the distillate when the oil running from the worm-end reaches a specific gravity between 1.010 and 1.030 at 60° Fahr. The length of time taken to work off this distillate will vary, of course, according to the volume of the charge and the nature of the tar; for a charge of 15 to 20 tons, 2½ to 8 hours may be taken as average figures. Yield per ton of tar is also chiefly affected by the nature of the tar, and may vary between 12 and 25 gallons. As a little more foul gas is given off during the working of this fraction, and its constituents are not so volatile as those of crude naphtha, it is advisable to increase slightly the pull on the foul gas main. The specific gravity of light oil may vary between 0.960 and 1.009 at 60° Fahr.

As the distillation proceeds, the oil running from the worm-end begins to appear more or less yellow in colour, and the smell of sulphuretted hydrogen, and other foul gases, gets a little stronger. A greater pull is put on the foul gas main, and more heat is applied to the tar. The temperature of the water in the condenser tank is kept elevated, as the distillate will still contain a fairly large quantity of naphthalene "salts." Frequently towards the end of this fraction the oil will show a tendency to set rapidly solid on cooling, due to a predominance of naphthalene "salts." This fraction is known as light creosote, middle oil, or carbolic oil, and, as the last name indicates, is one from which carbolic acid and its homologues are obtained. It is not the only one, however, as some tar acids are recovered from both the crude naphtha and light oil fractions. It is advisable to "cut" earlier for this fraction if the tar contains a large quantity of naphthalene. The point at which the distillate is "cut" to make this fraction varies between fairly wide limits, viz., when the specific gravity at the worm-end stands between 1.035 and 1.055 at 60° Fahr. and sometimes a little higher (1.060 at 60° Fahr.). According to various conditions, the yield per ton of tar may be between 8 and 13 gallons, and the specific gravity will range between 1.030 and 1.045. The length of time taken to work off this fraction, say from a 15- to 20-ton batch, falls between 1½ and 3½ hours.

As the process continues the distillate gets much yellower, the odour stronger, and the tendency to set solid on cooling sometimes decreases. More pull is necessary on the foul gas mains, and heavier firing is required to keep the distillate flowing from the worm-end in a thick. continuous stream. It is advisable to keep the water in the condenser tank hot, in spite of the general tendency shown by this fraction to remain liquid at more or less normal temperatures; sometimes it does not. To obtain what is known as the creosote or heavy creosote fraction, the distillate is "changed over" when the specific gravity at the worm-end is about 1.070 at 60° Fahr. It is difficult to give definite figures for the yield of this fraction, or of the length of time it takes to work off; they vary very much according to kind of tar worked, what is desired of the fraction, and so on. As a rough guide the yield may be taken as ranging between 28 and 35 gallons per ton of tar, and the time to work the fraction off a 15- to 20-ton batch, between 5 and 7 hours. The specific gravity may be within the limits of 1.050 and 1.065.

A stage in the process has now been reached in which the distillate has a very strong odour of sulphides, is of a greenish-yellow colour, and as it flows from the worm-end in a thick stream appears viscid. This fraction contains anthracene "salts" and is liable to bring about an obstruction in the condensing worm, unless the temperature of the condenser water is high. It is advisable to keep the water at about boiling-point. After this fraction has been running for a short time, the fire is slackened and steam is introduced into the still. The introduction of steam helps to lengthen the life of the still bottom by reducing the tendency of the pitch to coke. It also reduces the time required for the distillation, and, if carefully managed, increases the yield of oil. Passage of steam into the still is continued until the finish of the distillation, which point is determined according to the quality of the pitch required. It is not possible to give a definite point at which to introduce the steam; it will vary according to the quality of tar worked, and has to be found by experience. Roughly the introduction stage lies between the points at which the specific gravity of the distillate at the worm-end tests 1.070 and 1.090 at 60° Fahr. Care must be taken to use perfectly dry steam; wet steam, especially if inordinately wet, is liable to bring about a boil over. A convenient pressure to employ is 70 lbs. to the square inch. The steam valve must be opened gradually; steam must not be admitted into the still suddenly. It is advisable to let the fire die out, or shut off the gas, as the case may be, shortly before the finishing point is reached, the hot brickwork and the steam being sufficient to continue the distillation to the end. A still will continue to work for about half an hour to an hour after the fires are drawn, and if the precaution just mentioned is not taken, there is a risk of making the pitch too hard. According to the kind of tar being worked, or the quality of pitch required, the finishing point may vary between a specific gravity of 1.080 and 1.130 at 60° Fahr. The yield of this fraction, known as anthracene oil or "green" oil, given approximately as a guide, may be between 3 and 18 gallons per ton of tar, and the specific gravity may range from 1.070 to 1.100 at 60° Fahr.

When it is not desired to recover the anthracene, the heavy creosote and anthracene oil fractions are sometimes not separated but worked as one fraction. There are certain qualities of coal tar which yield so little anthracene oil that it is not worth while attempting to make a fraction. If it is desired to prepare a suitable creosote oil for burning in Wells or "Lucigen" lamps, then the heavy creosote distillate is "cut" at about 1.053 specific gravity at 60° Fahr., and a fraction collected between this point and 1.075 specific gravity at the same temperature. A good burning creosote must be absolutely free from insoluble matter and suspended naphthalene "salts." It should commence to distil at about 200° C., and approximately 60 per cent. distil over by the time 260° C. is reached. The specific gravity may vary between 1.065 and 1.070 at 60° Fahr.

In order that the stillman may test the distillate as it leaves the worm-end, he is provided with a No. 1 Twaddell hydrometer, a Fahrenheit thermometer with the scale inside (floating thermometers similar to those used in dairies are very suitable for the purpose), and some test jars. Tinned-iron test cans will prove more economical than glass test jars, which are easily broken. It is a good plan to arrange that the stillman has the "cut" or "change over" points given him at so many degrees Twaddell at 100° Fahr. This facilitates matters, and minimises the risk of overrunning the points, as the time taken for cooling the sample is less than if a lower temperature were used; and it saves the man making a calculation in cases in which the distillate sets solid above 60° Fahr.

If safety-valves are fitted to the stills, each of them should be examined and the valve given a twist on its seat to keep it in working order. This operation must be conducted while the stills are being charged, or before they commence to work. Syphon or U-pipes, if used in the stead of safety-valves, must be cleaned out and filled again with water before the distilling operation commences. A good method of cleaning these pieces of apparatus is to blow steam through them from a jet, which may be fixed in a convenient place on the top of the battery of stills. All the receiver mains should be blown out with steam immediately after the distillate has finished running through them, or at the latest soon after the distillation has ended. It is very advisable to clean out the foul gas mains at least once a week, by blowing through them with open steam.

The residue in the still (pitch) is allowed to remain for a varying period before running into the cooler. This is necessary in order to minimise the risk of damage to the still and its brickwork settings owing to the great heat stored up in them, to put less strain upon the cooler should this be of metal, and to reduce to a minimum the danger of the pitch taking fire. How long a period should elapse before "running off" the pitch will depend upon circumstances: for instance, whether the coolers are built of iron plate, or of brick, or constructed on the French weir system. The quantity of pitch in the still is another factor in the case. As a good average time 2½ hours may be taken; but the writer is acquainted with some cases in which 1½ hours is the full time allowed, and with others in which 6 or 7 hours are allowed to elapse before the running-off operation is carried out.

If the cooler is of the iron cylinder type, it must be prepared each time before running the pitch into it. Should it be fitted with a plug valve, the plug and seat must be cleaned and whitewashed. The plug must then be placed carefully on its seat, not jambed down too tight. Also the manhole should be covered properly with its lid, which may be lightly luted with lime putty. It is not necessary or advisable to fasten the lid down, for if it is left unfastened it will act as a kind of safety-valve. Sometimes the coolers are whitewashed on the inside, but this need not be done if they are arranged so that they drain well. Water must not be allowed to gain access to the cooler, as it may bring about trouble when hot pitch comes in contact with it. For this reason the manlid must be kept on during wet weather. Before releasing the pitch into the cooler, put a pull on the foul gas main. In hot weather it is a good plan to keep the outside of the cooler limewashed, if exposed to the sun's rays: it will retard the absorption of heat, and so not hinder the cooling.

When discharging the pitch from the still, the cock on the tail pipe should be opened very gradually. If the pitch does not run owing to its having set in the exposed portion of the tail pipe, and this sometimes occurs in very cold weather, then warm the pipe by placing under it a little tow soaked in creosote and igniting it. This must be done carefully. A sufficient time must be allowed for the still to thoroughly drain. To completely drain the still lowers the works expenses, as it reduces the amount of pitch coke formed at each distillation, increases the number of times a still can be worked before cleaning, and minimises the amount of wear on the still bottom. It is not necessary, nor is it advisable, to remove the manlid of the still before discharging the pitch; nor need any of the connections be taken apart. The foul gas main connected to the coolers should be kept at work for between one and two hours after the pitch has been discharged into them.

After the still has been discharged, it must be allowed to stand empty for a period, the length of which will depend upon the size of the still and whether it is provided with a preheater or not. If there is no preheater, the flue dampers must be opened, in order to allow a current of air to pass round the still and cool it. After the elapse of between 1½ and 2 hours the still can then be charged with cold tar. It is not advisable to shorten the time, as this will introduce the risk of an explosion, and also bring about an undue strain on the rivets and seams, producing leaks. In cases in which a preheater is provided there is no need to draw the dampers, and the still may be charged again about half an hour after the pitch has been run off. The tar in the preheater being hot the danger of starting the seams, or of explosion, is avoided. Whether cold or hot tar is run into the still it is as well to commence the operation slowly, and increase the speed of flow, say after about 5 or 10 minutes has elapsed. Before commencing the next distilling operation, it is as well to dip the still, to check the amount of the charge.

The pitch is allowed to remain a number of hours in the cooler before it is discharged on to the bay. It is not possible to give a definite time, as the size of the cooler, requirements of local by-laws, state of the weather, and other conditions will affect this. In any case, it is not advisable to run the pitch on to the bay too hot; some of the volatile matter is lost thereby, and acrid vapours are given off in such dense clouds that they create a nuisance. A good temperature at which to release the pitch is 260° Fahr. When there are several coolers to discharge, it is best to release one of them at a time. Arrangements should be made to run the pitch on one portion of the bay only, by this method allowing a previous running to cool while another section is being dug. The pitch must not be run on to the bay too thickly: 12 to 18 inches is an ample depth. Much above this thickness will take an excessive time to cool, and is not dug so easily.

Before running off the pitch from the coolers the bay must be properly prepared to receive it. It is necessary to lime or chalk-wash the bottom and the sides if these are of brick or concrete. Sand must not be used; the buyers do not appreciate it. The very thinnest wash of lime or chalk-milk is all that is necessary. Every endeavour must be made to keep water off the bay, at least just previous to the discharging operation and while that is going on. The effect of water on hot pitch is to fill it with vapour cells, or in other words to make it cellular. This appearance is not sought after by buyers. There is of course the difficulty of coping with wet weather. The best plan to adopt on a wet day is to lime-wash the bay a few minutes before discharging the pitch, and then run it on to the bay as quickly as possible. If the pitch is run to the bay via a gutter, see that the gutter is limewashed and cleaned out after each operation.

After a still has been worked a number of times, varying according to the state of the tar, the care with which the still was set, and the amount of draining after each operation, it must be cleaned. A good average is seven times; often a still is cleaned after working four times, and cases occur in which it is not cleaned until it has worked eighteen times. The money and time spent in *frequent* still cleaning cannot be considered as wasted. It brings about a saving in fuel and increases the life of the still bottom, both to a considerable degree. In the cleaning operation, the mixture of partly coked pitch and free carbon must be cleaned or scaled off the still bottom and sides very thoroughly, taking care to remove any which may adhere to rivet heads or find lodgment in seams. The formation of this scale is due partly to the heat retained in the brickwork surrounding the still coking the thin layer of pitch left in the still at the end of the " running off " operation, and partly to " free carbon " which deposits and adheres to the bottom during the first and intermediate portions of the operation. For the scaling of stills, the following tools are in general use: short or miner's picks, straight and cross pane 4-lb. hammers, and chipping chisels.

It is very necessary that certain precautions be taken to prevent accidents to workmen during the cleaning process. The still should be completely isolated from adjoining plant by disconnecting the swan neck from the condenser worm and the tail pipe from the pitch cooler. If there is not a small connecting pipe which can be removed completely, then a blank flange should be placed between the disconnected flanges. In cases in which the still is connected to a preheater the cock on the charge pipe must be locked or a blank flange used, as just described, on the still side of the cock. The manlid must be removed shortly after the pitch has been run off, and it is as well to drive out the foul air by blowing steam into the still. Sufficient time must be allowed for the still to cool before an entry is attempted. The length of time will vary according to the size of the still, the time of the year, and whether the still is one of a battery or the only one. It is best found by experience, but as a guide, 30 to 48 hours are general in tar-distilling practice. A responsible person should inspect the still before a workman is allowed to enter. The workman who enters the still must have a belt fastened round his body, with a rope attached. This belt is best made of stout webbing, and provided with two wash-leather pads on the spots which come under the armpits. In order that the wearer may be drawn up head-foremost in a case of "gassing," the belt must be worn well up to the armpits. Two men should be on duty outside the still, having charge of the free end of the rope and keeping watch on the workman inside for any signs of " gassing." The ladder which is used to descend into the still is provided with two straight hooks at the top, which fit over the manhole edge, and thus prevent slipping.

Prepared and dehydrated tars are used for many purposes, the chief of which is for road treatment. Among the minor uses may be mentioned its employment in the manufacture of roofing felt, electric arc-lamp carbons, and the linings of converters used in the basic Bessemer process. Most of the specifications to which these prepared tars are made are the private property of interested firms.

Dehydrated tar is made without difficulty by distilling off carefully all the water (entangled ammoniacal liquor) and with it, of course, the crude naphtha, from a charge of coal tar. After these products have distilled off, the fire is drawn, dampers opened, and the still allowed to rest for a few hours, when the dehydrated tar may be pumped into a storage tank, railway tank wagons, or filled into barrels. The connection between the still and the cooler must, of course, be broken, and the tail pipe of the still fitted up to a main connected to a pump, and also by-passed to a barrel filling stand-pipe. Sometimes tar which has been kept in stock for a considerable time is called dehydrated tar, but in the strict sense this is not a correct term, as this kind of tar will contain a certain percentage of entangled water, in spite of long standing.

As already mentioned, by far the greater quantity of prepared tar is used for road treatment, and therefore chief consideration will be given to it in this connection. A batch of prepared tar, suitable for road treatment, may be manufactured as follows. Twenty tons of gas tar are charged into a still, and the ammoniacal water, crude naphtha, light oil, and middle oil distilled off, as described on pages 72–74. When the distillate at the worm-end reaches a specific gravity of 1.045 at 60° Fahr. the fires are drawn, or the gas shut off, and the dampers opened. The contents of the still are allowed to stand at rest until the temperature reaches about 250° Fahr., and then 2300 gallons of heavy creosote of a specific gravity between 1.060 and 1.065, and free from "salts" and water, are added. Thorough agitation of the mixture is necessary. The creosote is added by pumping it through the tail pipe of the still, and agitation is brought about by blowing a gentle current of air into the still through the same pipe. A far better plan, and one which will not hold the still up while the half-finished material is cooling to 250° Fahr., is to provide a cylindrical boiler tank of suitable size as a mixing tank, and run or pump the material from the still into this. It should, of course, be allowed to rest for an hour or two in the still before running into the mixing tank. This tank can be fitted with a mechanical agitator, or the agitation be carried out by blowing air into the material through a perforated pipe. After a thorough mixing, the prepared tar may be pumped into railway tanks or to a storage tank, or filled into barrels for despatch. As it is often required that the prepared tar be filled into tar spraying machines hot, it is a good plan to place the storage tank in an elevated position, and provide it with a closed steam coil. By this means the tar can be run into the spraying machine by force of gravity, and hot. The specific gravity of prepared tars may vary between 1.16 and 1.125 at 60° Fahr.

During the last few years there has been a considerable amount of discussion on the subject of tar preparations for road treatment. The Road Board issued in April 1911 a set of general directions and specifications relating to the tar treatment of roads, and these directions and specifications were revised in 1914. The chief items in the tar specifications of interest to tar distillers are those which relate to: (*a*) the source of the tar; (*b*) the specific gravity; (*c*) freedom from water; (*d*) fractionation; (*e*) amount of phenols; (*f*) free carbon content. Briefly, the specific gravity must be high, the amount of water and phenols soluble in water low, and the free carbon must not be higher than 20 to 21 per cent. If the reader desires further particulars he is referred to the literature on the subject, among which are the publications mentioned in the footnotes.[1]

The experience of practical tar distillers, which the writer can corroborate, shows that it is not possible for the tar distiller to produce from some crude tars a prepared tar that will answer the specifications laid down by the Road Board; and yet tars can be manufactured at these works which, when used on roads, give results equal to any that answer the Road Board specifications. For example, the four tars A, B, C, and D in Table XV have been used largely for road treatment, all of them giving excellent results, and yet when compared with the Road Board specification only C and D answer it.

TABLE XV

ROAD TARS

	Road Board specification.	A tar.	B tar.	C tar.	D tar.
Below 170° C.	not more than 1 %	nil	¼ %	nil	nil
170–270° C	not less than 16 % not more than 26 %	30 %	29 %	25 %	22 %
270–300° C	not less than 3 % not more than 10 %	7 %	9 %	10 %	4 %

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[1] *General Directions and Specifications relating to the Tar Treatment of Roads*: Road Board. Waterlow & Sons, Ltd.

"Improvements of Highways to meet Modern Condition of Traffic," by T. W. Smith. *Proc. Inst. C.E.* Series 1910-11.

"Up-to-date Roads," by R. O. Wynne Roberts. *Trans. Socy. Engrs.*, May 1910, vol. i. No. 5.

"Investigations on Coal Tar and some of its Products," A. R. Warnes and W. B. Southerton, *Trans. Midland Junior Gas Association*, As a matter of fact A tar has been used on roads subjected to very heavy traffic and it has stood well for a period of two years.

TABLE

	Tar No. 1.	Tar No. 2.
Use	Surface tarring of roads.	For making tar macadam, or surface tarring of roads in very hot weather.
Origin	Bituminous coal alone, or with not more than 10 per cent. of its volume of tar, etc., produced in manufacture of carburetted water-gas.	Bituminous coal alone, or with not more than 25 per cent. of its volume of tar, etc., produced in manufacture of carburetted water-gas.
Specific gravity at 59° F.	1.16 to 1.22.	1.19 to 1 24.
Content of water	Not exceeding 1 per cent. by volume; the water present not to contain more than 5 grains total ammonia per gallon of the tar.	.. ..
Fractionation from one-litre flask		
Distilling below 338° F.	Not more than 1 per cent. light oils.	Not more than 1 per cent. (light oils and water, if any).
Distilling between 338° and 518° F.	Between 16 and 26 per cent. middle oils. This shall remain free from solid matter when kept at 86° F. for 30 minutes.[1]	12 to 18 per cent. Shall remain clear when kept at 77° F. for 30 minutes, and not contain more than 2 per cent phenols.
Distilling between 518° and 572° F.	Between 3 and 10 per cent. heavy oils.	6 to 10 per cent.
Total distillate between 338° and 572° F.	Between 24 and 34 per cent.	21 to 26 per cent.
Distillate between 518° and 599° F.	.. ..	.. ..
Free carbon	Between 12 and 21 per cent. by weight, when extracted by benzol and carbon disulphide. (Residue from extraction is "free carbon.")	12 to 22 per cent. by weight.

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[1] This requirement may be waived in the case of tar direct from gas-works, but tar from which the naphthalene has been extracted is preferable to tar containing much naphthalene. This "middle oils" distillate is required further not to yield to caustic soda more crude tar acids (phenols)

The following specifications (Table XVA) for tars, pitches, and tar oils have been issued by the Road Board (2nd Edition, 1914):—

XVA

Prepared pitch from tar distilleries.	Commercial soft pitch.	Tar oil.
Pitch grouting	Pitch grouting	For softening commercial soft pitch for pitch grouting.
..	As for Tar No 2	A filtered green or anthracene oil: origin as for Tar No. 2.
.. ..	.. ..	1.065 to 1.085 at 68° F.
.. ..	.. ..	Shall be commercially free from light oils and water.
.. ..	.. ..	Not more than 1 per cent. (light oils and water, if any).
Not more than 1 per cent. distillate below 518° F.	Not more than 1 per cent. distillate below 518° F.	Below 518° F., not more than 30 per cent. (middle oils, light oils, and water).
.. ..	.. ..	.. ..
.. ..	.. ..	.. ..
.. ..	2 to 5 per cent.	Below 626° F., not less than 96 per cent. total distillate.
16 to 28 per cent. by weight.	18 to 31 per cent. by weight.	.. ..

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than is equivalent to 3 per cent. of the tar (by volume). The original publication (Waterlow & Sons, price 8d.) should be consulted for details of the method of distillation, etc.

Some manufacturers of road tars advocate the addition of crude naphtha to these preparations. This should not be tolerated, as crude naphtha is a valuable benzol, toluol, and naphtha yielding material. If ever middle oils are employed in the manufacture of road tars they should be deprived of the useful phenols first.

A tar for the manufacture of roofing felt may be prepared by distilling a charge of coal tar until the distillate at the worm-end tests 1.050 at 60° Fahr. The distillate which comes over before this point is reached is separated into the usual fractions as already described. The residue is allowed to cool to about 240° Fahr. either in the still or in a suitable mixing tank, and then mixed with creosote of a specific gravity 1.045 at 60° Fahr., in the proportion of 1750 gallons for every 15 tons of tar distilled.

The processes of continuous dehydration and continuous distillation of tar as carried out when using the Hird plants described in Chapter V. will now receive attention. In the continuous dehydration plant the following takes place. On leaving the storage tank the crude tar enters the condenser tank by the tar inlet at the bottom, and in passing upwards to the outlet on the opposite side of the tank circulates round the condenser coil and absorbs heat from the distillate which is passing through this coil on its way to the distillate receiver. After leaving the condenser tank the crude tar passes through the inner tube of the cooler, and while doing this it absorbs heat and cools the prepared tar which is flowing through the cooler jacket on its way to the prepared tar receiver. From the cooler the hot crude tar enters the still at a temperature approximating 70° C., and travels first down one side and then up the other, due to the presence of the central longitudinal baffle. While the tar is passing through the still it is heated by the four bunsen burners working in the tubes at the still bottom, and it gives off in the form of vapour the crude naphtha, light oil, and carbolic oil, which pass forward through the swan neck and vapour pipe to the condenser coil, where they are condensed, and from which they are conducted in the liquid form to the distillate receiver. The tar leaves the still, passes into the jacket of the heater, and thence into the prepared tar receiver.

The continuous process of tar dehydration offers several advantages over the intermittent system, among which are (1) low supervision charges, (2) low fuel consumption per ton of tar distilled, (3) reduced wear and tear of plant, (4) small area occupied by plant, (5) low cost of plant. Continuous dehydration plants can be considered satisfactory for the removal of the benzol and toluol which are taken up by the tar in the gas-washing process. They are also very suitable for the preparation of prepared tars to answer the Road Board specifications. It is, of course, necessary to vary the working temperature according to the kind of prepared tar required. For tar to answer specification No. 1 for spraying, the working temperature approximates 230° C.; for specification No. 2, tar for macadam, a working temperature of 260° C. is necessary, and for specification No. 3, tar for grouting, a temperature of 288° C. is the best to employ. Naturally the character of the prepared tar and the yield of distillates will vary a little according to the quality of the crude tar passing through the plant. The fuel consumption is very low; for instance, in the case of the Hird plant, in making No. 2 Road Board specification tar at a working temperature of 260° C., 1 ton of tar required 67 lbs. coke breeze, or if gas-heated, 550 cubic feet of gas at 500 B.Th.U. The finished tar on leaving the plant has a temperature of from 230–260° C., and on flowing through the heat interchanger heats the ingoing tar to approximately 100° C. Crystallisation of naphthalene in the light oil need not be feared as this distillate leaves the condenser and passes through the seal box at a temperature sufficiently high to prevent it.

Compared with the intermittent system, Hird's continuous system of tar distillation shows several advantages. The chief of these are:—

(1) When started the plant is able to do its work automatically, without depending entirely upon personal supervision.

(2) Very low temperatures prevail throughout the whole of the stills, with the result that wear and tear of plant is reduced to a minimum.

(3) Priming troubles are entirely eliminated, with the result that the various distillates are very light in colour, and leave little residue on re-distillation.

(4) The process being continuous, there is no loss of heat from stopping and restarting and, consequently, there is a distinct economy in the cost of distillation.

(5) The various fractions are automatically and simultaneouly discharged into the receivers, and no attention whatever is necessary in this respect.

(6) The size of the plant is approximately one-quarter that of the intermittent tar still for the same output. A plant to deal continuously with one ton of tar per hour never contains more than 3 tons of tar in process of distillation.

Briefly, the method of working this plant (see Figs. 38-42) is as follows: The crude tar is conducted from the storage tank into the regulating tank, and from this tank it flows to the first of a series of four heaters, a constant head being maintained by means of a float valve in the regulating tank. On passing through these heaters the temperature of the tar is raised by its receiving heat from the distillates leaving the stills as they pass through the coils. During its passage the tar is deprived of some of its water and crude naphtha. The vapours of these materials pass into a common main and thence through the coil of a coil condenser, in which they are condensed. The condensed liquids pass through a sight box and a separator, and then to their respective receivers.

After its passage through the heater-coolers the tar flows through the pitch cooler, and while doing this its temperature is further raised, while that of the pitch is correspondingly lowered. On leaving the pitch cooler the temperature of the tar is approximately 126° C., and at this temperature it enters No. 1 still. Here the balance of the ammoniacal liquor and crude naphtha are distilled off. Leaving No. 1 still the tar enters No. 2 still, in which its temperature is raised to about 249° C., and during its passage through this still the light oil is distilled off. Entering No. 3 still its temperature is raised to approximately 340° C., and at this temperature the creosote oil comes over. Passing from this still the partly distilled tar enters No. 4, in which its temperature is actually reduced, falling approximately to 260° C. This reduction is effected by the employment of injected steam, no other means of heating being employed in this still. The tar is in fact submitted to a steam distillation which brings over the anthracene oil at a much lower temperature than would be necessary if fire heat were employed. This effects a considerable saving on the plant from a wear-and-tear point of view.

The residue in No. 4 still is liquid pitch, and this passes from the still into the pitch cooler, through which it travels on its way to the pitch bay, and during its progress it gives up much of its heat to the crude tar passing through a pipe immersed in it on its way to No. 1 still. The temperature of the pitch on leaving the cooler is such that it does away with the giving off of the white irritating fumes so often observed when running off pitch in the intermittent system.

With this plant it is possible to adjust the temperatures so as to obtain continuously uniform fractions of any desired boiling-point, while at the same time the pitch can be varied to meet any desired twisting point. One man is able to superintend the working of the plant, his duty being merely to adjust the burners and read the thermometers, which indicate clearly the working of the stills.

To enable the works manager to keep some sort of check on the yield of the various distillates obtained from the tar which he is passing through his stills from month to month, it is a good plan to make out a balance-sheet, say once a week, similar to the following :—

	Tons.		Galls. per Ton.	Tons.
Tar distilled	100	Liquor	5.86	3.00
		Crude naphtha	3.83	1.56
		Light oil	16.80	7.57
		Middle oil	9.68	4.47
		Creosote	29.40	13.72
		Pitch	--	67.78
		Loss (by difference)	—	1.90
	100			100.00

Ultimate Products

Benzol, 90 %		1.71 galls. per ton tar.
Solvent naphtha, 90–160°		2.06 ,, ,, ,, ,,
Heavy naphtha, .920		0.45 ,, ,, ,, ,,
Carbolic, 50°		4.03 ,, ,, ,, ,,
Creosote—		
From tar direct	39.08	
From bottoms	14.39	53.47 ,, ,, ,, ,,
Pitch		13.55 cwts. ,, ,, ,,

Working costs in regard to the distillation of tar will vary in different works according to local conditions, kind of tar, type of plant, condition of plant, whether gas or coal firing is employed, and so on. The following figures may, however, prove of some use as a guide to beginners.

Wages productive and non-productive, 2s. 6d. per ton of tar distilled.

Stillman's wages, 4½d. per ton of tar distilled.

CHAPTER VII

PLANT FOR RECOVERING CRESYLIC AND CARBOLIC ACIDS FROM OILS

Sulphuric acid process—washers—storage tanks—springing tank—CO_2 process—carbonating boilers—phenolate tanks—pump and sump—reaction towers—divider tanks—receivers for tar acids—receivers for spent liquor—finishing tank—acid egg—storage tanks—CO_2 gas—CO_2 furnaces—purifying and washing towers—water separator—causticising plant—causticisers—storage tanks—filters—pump—evaporators—cresylic acid—still charging tank—still—fractionating tower—condenser—" bottoms " receiver—pitch bay—cresylic and carbolic receivers—air blowing tank—continuous tar acid extraction plants

THERE are two methods in general use for the recovering of phenols from tar distillates: (*a*) The sulphuric acid process, in which moderately dilute sulphuric acid is used to decompose the solution of phenolates—known technically as " carbolate " and " cresylate "—and the resulting sodium sulphate run to the drain, the phenols only being recovered; and (*b*) the CO_2 process, in which carbonic acid gas is employed to decompose the " carbolate " or " cresylate," the resulting sodium carbonate being converted into caustic soda by causticisation, and used for extracting a further quantity of tar acids. The latter process is sometimes known as the " continuous process." It is much more economical to work than the former, although the initial outlay for plant is somewhat greater.

Washing tanks, generally known as washers, are required for both processes. These tanks may have a total capacity of 3500 to 4500 gallons, and in shape are generally cylindrical; sometimes round-bottomed, trough-shaped tanks are used. The cylindrical washers are placed in a horizontal or vertical position. If in the former position, the washer should be tilted a little towards the outlet, but if in the latter, it should be provided with a dish or shallow cone-shaped bottom. A cone-shaped bottom will give the best results as regards draining. Horizontal washers are provided with a shaft on which are fitted agitating arms, and the journals of which pass through stuffing boxes let in each end of the washer. Good second-hand boilers, from which the tubes have been drawn and the ends blanked, make excellent washers. Vertical washers may be fitted with an archimedean screw agitator, or wing agitators, on a horizontal or vertical shaft. If an agitator of the latter type is used in the vertical position it is advisable to fit several fixed arms on the side of the apparatus. It is policy to cover the vertical and also the horizontal trough-shaped washers, and a manhole and lid must be provided. A useful piece of apparatus to employ in connection with the washer is an oil separator. This is similar in pattern to the divider box described on page 53, Fig. 30, but it is often made a little larger. The object of using this piece of apparatus is to separate any oil from the final runnings and drainings of "carbolate" or "cresylate," a matter of some importance. Any oil which may come with the ammoniacal liquor, which it is sometimes necessary to draw off before commencing a wash, may be recovered if a separator is used.

With the exception of "carbolate" and "cresylate" storage tanks and tar acid storage tanks, which may be of any shape and size to suit circumstances, a "springing" tank is the only other piece of plant required in the sulphuric acid process. The "springing tank" may be constructed of wrought-iron plate, but even if care is used in conducting the process, some corrosion of the plates, and, if mechanical agitators are fitted to the tank, of the agitators, will take place. Lead-lined iron or wooden vessels are more suitable for this part of the process. It is now possible to obtain iron vessels homogeneously coated with lead, covered, and provided with an agitator. A vessel of this kind is very suitable for the "springing" of carbolate. Covered tanks provided with mechanical agitators are safer to use than uncovered tanks, the contents of which are agitated by hand. Wooden agitators are usually employed for hand agitation. The shape of a "springing" tank may be cylindrical, or like a round-bottomed trough. Cylindrical tanks may be placed horizontally or vertically. If in the latter position, and this is really the best, a dished or cone bottom should be fitted to the tank. This will allow of a better draining of the tank from the sodium sulphate liquor which separates after "springing." The cock fitted to the bottom of the tank to run off the contents should be made of acid resisting metal, such as regulus metal or "Tantiron," for preference. Some people prefer to skim the tar acids off the surface of the sulphate liquor, but this is not so cleanly as running first the sulphate liquor and then the tar acids from a bottom cock. The capacity of a "springing" tank may vary between 1000 and 2000 gallons, sometimes even greater, but a good average figure may be taken as 1500 gallons.

For working the CO_2 process more plant is required than that just described for the sulphuric acid process, and it is of a somewhat complicated nature. In addition to the washing tanks, the following are necessary: Two "carbolate" or "cresylate" boilers, a pump and suction sump, a reaction tower, two dividing tanks, a receiving tank for the tar acids, a receiver for the spent liquor (impure carbonate of soda solution), one finishing tank, one acid egg, one furnace for generating CO_2, a dust separating apparatus and tower for purifying and washing the CO_2, and the necessary pipe lines and arrangement for removing the water which sometimes separates from the gas. The gas may be drawn through the apparatus by the employment of a steam jet. According to the requirements of the Alkali Act, the spent gas must be purified before passing to the atmosphere. This can be done by passing it through one or other of the well-known purifiers, and then allowing it to escape into the chimney stack, or it may be passed over the steam boiler fires, after travelling through a seal pot, as described when dealing with foul gas mains, pages 55, 56, Fig. 32.

Instead of employing a reaction tower, some distillers prefer to put in what are known as carbonating boilers. The number of these boilers required will vary according to the volume of "carbolate" to be dealt with, but it is advisable to put in at least four. No large divider boxes, receivers, or pump and sump, are necessary if carbonating boilers are used. Of course a pump for removing the spent liquor is required in both cases. The CO_2 is forced through the "carbolate" or "cresylate" via perforated coils, by means of a compression pump, and the acids which separate are either removed from the boilers by means of skimmer pipes, or the contents of the boilers are run into tanks with open tops, and after standing for a sufficient time, the acids are removed by skimmer pipes. If desired the separation of the acids from the spent liquor may be carried out by running off from a bottom cock first the spent liquor and then the tar acids. When nearing the line of separation it is wise to run the liquid through a small dividing apparatus (p. 53, Fig. 30), thus avoiding any loss of acids.

Dealing with the CO_2 process, in which a reaction or carbonating tower is used, the pieces of plant named will be described in the order given.

The "carbolate" or "cresylate" tanks are constructed of wrought-iron plates. Second-hand, cylindrical boilers, if in good condition, make excellent tanks for this purpose. Whether new or second-hand tanks are used the joints must be well caulked, or leakage will take place. A hole is cut in the top to admit a 1½- or 2-inch inlet pipe; two smaller holes are cut, one for the admission of a 1-inch steam-pipe, to which is connected a double-lap closed steam coil, and the other to allow the exit of the exhaust pipe of this coil. Both these holes should be at the top of the boiler-tank. The manhole and cover are allowed to remain: a manhole is sometimes useful for cleaning or inspection purposes. At one end of the boiler tank a 1½-inch hole is cut the centre of which should be 3$\frac{3}{4}$ inches from the bottom of the tank, and a 1$\frac{1}{2}$-inch pipe is fitted by means of a flange. This pipe is to conduct the phenolates to the pump sump. A cast-iron gland cock is fitted near the end of the pipe to regulate the flow into the sump, and it is wise to fit a further cock a few inches from the tank as a safeguard in case of accident. It is a good plan to arrange for a steam connection into this pipe in order to assist in removing any obstructions which may occur, and provision for the insertion of an open steam end into the tank is an advantage. At the opposite end of the boiler-tank a small mud-hole 6 inches by 4 inches should be cut. The lower edge of the hole must be as near the bottom as possible, and a casting should be riveted on to carry the mud-hole cover. Both tank boilers may rest on 14-inch to 18-inch brick cradles, just a few inches above the ground level. The capacity of these tanks will vary, of course, according to the quantity of tar acids it is desired to make per day

The pump may be of any good make, and the delivery vary between 1 inch and 1$\frac{1}{2}$ inches according to circumstances. It is erected a few inches from the ground level, in close proximity to the sump. A cast-iron vessel, about 2 feet deep and 1 foot in diameter, makes a suitable sump; a wrought-iron steam boiler dome will answer admirably. The sump is situated so that the top rises about 3 inches from the ground level, and if out-of-doors a wooden cover should be provided to keep rain out. A few inches of puddle should be put in the hole before placing the sump into position.

There are two chief types of reaction or carbonating tower: the packed and the plate. The latter kind of tower is built up of cast-iron sections, while the former is constructed of wrought-iron plates. One of the best designs of plate tower is illustrated in Fig. 43. Naturally the size of the tower will vary according to the quantity of phenolate it is desired to decompose per diem. It may be approximately 15 feet high and 2 feet in diameter, the sections being 8$\frac{1}{2}$ inches deep over all. The number of dispersers in each section will vary according to its diameter. In a section of 2 feet diameter 8 may be put in, the inlets to the dispersers being 1$\frac{1}{2}$ inches internal diameter and the diameter of the disperser hoods 4 inches. Each hood should have 12 by $\frac{1}{2}$-inch openings in the circle. Only one internal drain-pipe of 1$\frac{1}{2}$-inch bore is necessary for each section. This pipe should be arranged to allow a seal of 1$\frac{3}{4}$ inches of liquid on each plate. It is an advantage to provide an inlet for a steam-pipe so that the tower may be steamed out occasionally. The positions of the gas inlet and outlet, and also of the outlet for the spent liquor and tar acids, are shown in Fig. 43.

A packed reaction or carbonating tower is filled with foundry

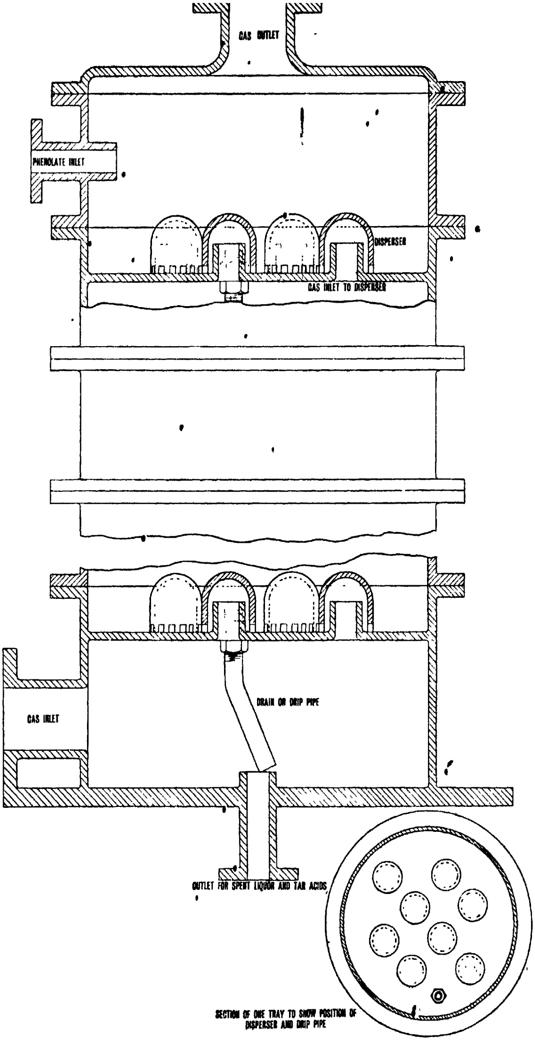
GAS OUTLET
PHENOLATE INLET
DISPERSER
GAS INLET TO DISPERSER
DRAIN OR DRIP PIPE
GAS INLET
OUTLET FOR SPENT LIQUOR AND TAR ACIDS
SECTION OF ONE TRAY TO SHOW POSITION OF DISPERSER AND DRIP PIPE

FIG. 43.—Carbonating or Reaction Tower—Plate Type.

coke, earthenware balls, tiles, or one of the numerous patent tower packings. To pack a tower for this kind of work with coke is in the writer's opinion a mistake: the coke soon becomes clogged and the available reaction surface is thereby much reduced. Often it clogs into hard masses, leaving fairly large holes here and there, called "rat holes," up which the gas travels, coming in contact with only the outside portions of moderately thick streams of liquid flowing in the opposite direction. Earthenware balls alone, or with small granite chips, in the writer's hands, have given excellent results. In choosing a packing for a reaction tower of this kind, due regard should be given to the question of reaction surface: the greater this is the more rapid will be the decomposition. Three-inch earthenware balls with ½-inch hole give approximately 14.5 square feet of reaction surface per cubic foot of tower space; 2-inch balls with ½-inch hole, 23.3 square feet; and 1-inch balls with no hole, 37.3 square feet. Small granite chips, about 1 inch by ½ inch by ½ inch approximately, will give a very considerable reaction surface; about 100 square feet per cubic foot of tower space may be taken as a guide. A tower to deal with 2500 gallons of phenolate solution, containing 20 per cent. of tar acids, per 24 hours, would require to be about 13 feet high and 4 feet in diameter, if packed with 1-inch balls with no hole, or if 2-inch balls with ½-inch hole are used, the height of the tower may be 22 feet and the diameter 4 feet. If packed with 3-inch balls with ½-inch hole, a height of 27 feet and a diameter of 4 feet 6 inches would be necessary; or if 4 feet of small granite chips and 18 feet of 3-inch balls were used as packing, then the height of the tower could be reduced to 25 feet, the diameter remaining the same. These figures are given as a guide, and may of course be varied according to requirements. The wrought-iron plates of which the tower is constructed need not be thicker than ⅜ inch; ¼-inch plates are often used. If balls and granite chips are used together, two perforated plates are required, one as a false bottom and the other to rest on the top of the balls to support the granite chips. If balls are used alone, then one plate for the false bottom is all that is necessary. The plate for the false bottom should be ¾ inch to 1 inch thick with ½-inch holes at 1-inch pitch, and supported on cross-bars about 1 foot 6 inches from the bottom of the tower, but the top plate need not be more than ¼ inch thick, the holes being of the same diameter and at the same pitch. Cast-iron is the best metal to use. In the top or cover plate of the tower, a 4-inch hole should be cut for the gas outlet pipe, a hole for a manhole of the usual size, and one for the phenolate delivery pipe, which latter leads to a spray arrangement. A 4-inch gas inlet is made with the centre at least 5 inches from the bottom of the tower and to this a screwed flange is fitted. The end of the gas pipe is introduced through this flange so that 3 or 4 inches project on the inside. An inlet for a 1-inch steam-pipe to admit steam for steaming out the tower occasionally is made with its centre about 8 inches from the bottom of the tower, and in the bottom plate an outlet, about 1½ inches in diameter, is provided for the pipe which conducts the mixture of spent liquor and tar acids to the divider tank. The spray arrangement may be of the Gurney type (see Fig. 44), or built up of a 6-way piece connected to the delivery pipe inside the tower, and into which are screwed 6 lengths of ½-inch wrought-iron pipe, about 22 inches long, and perforated with ¼-inch holes on the under side at a pitch of approximately 5 inches. These holes should be in alternate positions when one pipe is compared with the next. Details of the method of packing this type of tower, and the arrangement of the pipes, are shown in Fig. 45.

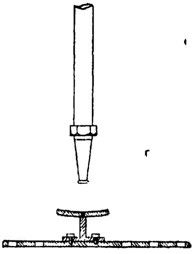
FIG. 44.—Gurney's Jet arranged for Carbonating Tower.

The divider tanks are made of wrought-iron and much larger than those used in the tar distilling plant. They are generally constructed square in plan, and the depth nearly twice that of the width. An average size is 2 feet 3 inches by 2 feet 3 inches by 4 feet deep, ¼-inch wrought-iron plate being used, the seams thoroughly caulked, and an angle rim placed outside. In order to promote the forward flow of separated spent liquor one divider tank is set about 9 inches higher than the other. The pipe to the tar acid receiver which is attached to the first or separating tank is of 1-inch wrought-iron pipe, and it is connected to a movable syphon pipe as shown in the diagram (Fig. 46). The lower tank is really a catch tank, which retains any tar acids escaping from the divider, and the pipe from the separating tank which leads the separated spent liquor to this tank and also the pipe which conducts the spent liquor from the catch tank to the spent liquor receiver are of 1½ inches wrought-iron. Any tar acid which separates in the catch tank, and it should be very little, is removed by skimming. Reference to Fig. 46 will give the method of fixing and other details.

A wrought-iron riveted tank, square, rectangular, or cylindrical in shape, may be used for the tar acid receiver. It should be placed near the divider tanks, and, if in the open air, covered in, a lid being provided in the cover in order to make inspections. The outlet pipe, which is of 1-inch wrought-iron, is with advantage connected with a movable skimmer pipe, as generally on standing some spent liquor separates from the tar acids and settles to the bottom. In order to facilitate this separation, and thus save some sulphuric acid, a closed steam coil may be placed at the bottom of the tank and fed with exhaust steam. The tar acids should be kept at a temperature not exceeding 75° Fahr. As regards the size of the tank, this will of course vary according to the volume of tar acids it is desired to deal with per day. The tank may be erected on the ground level, or raised several inches, according to circumstances.

The receiver for spent liquor should be of wrought-iron, and a good-quality second-hand steam boiler answers admirably. It should be placed partly or wholly below the ground level, according to circumstances. The hole must be lined with well-made puddle before putting the tank in. A manhole with tight cover, a dipping pipe which also makes an air vent, and holes for inlet pipe and suction pipe, are required. The dipping pipe should reach about 9 to 12 inches above the ground level, and need only be ¾-inch internal diameter, the inlet pipe hole 1½ inches, and the suction pipe 2 inches. If the

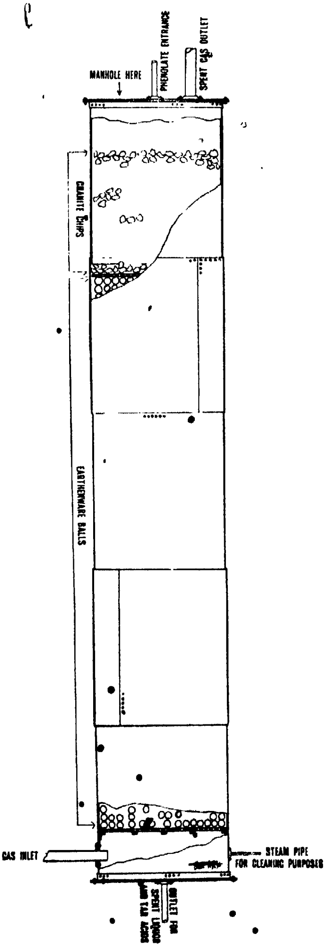

FIG. 45.—A Cylindrical Carbonating Tower, Packed Type.

tank is only partly below ground, the dipping pipe is not necessary: a $\frac{3}{4}$-inch hole will suffice.

A lead-lined tank must be put in for the purpose of carrying out the finishing operation. The tank may be rectangular or square in plan, and built of well creosoted timber, lined on the inside with stout "chemical" lead. Five or seven pound lead is quite thick enough. There is no need to provide for any openings in this tank, as the finished acids can be most conveniently removed to the acid egg by means of an ever-ready syphon (Fig. 47). The tank should be placed as near to the acid receivers as possible, and on the ground level.

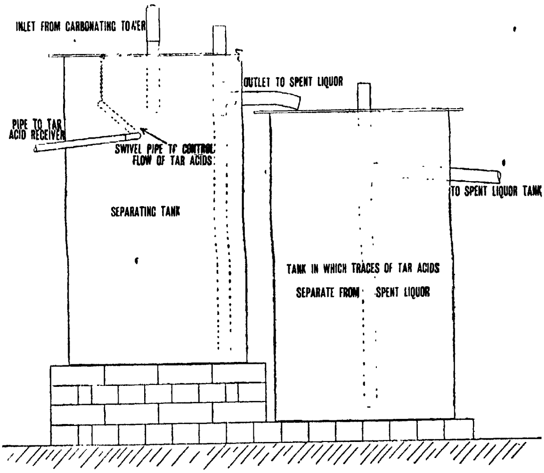
INLET FROM CARBONATING TOWER
OUTLET TO SPENT LIQUOR
PIPE TO TAR ACID RECEIVER
SWIVEL PIPE TO CONTROL FLOW OF TAR ACIDS
TO SPENT LIQUOR TANK
SEPARATING TANK
TANK IN WHICH TRACES OF TAR ACIDS SEPARATE FROM SPENT LIQUOR

FIG. 46.—Divider Tanks, CO_2 Tar Acid Recovery Process.

The acid egg may be constructed of cast-iron, wrought-iron, or lead. Of the three metals, lead is the least likely to suffer from corrosion, but to construct a large egg, say of a capacity of 150–200 gallons, is an expensive matter. Cast-iron is liable to fracture, and in the writer's opinion a wrought-iron egg will give excellent results and suffer very little corrosion if properly managed. There is no difficulty in making a wrought-iron egg of large size, and it is cheap. If the ends are well dished, there is no need to put in a central stay, which is of course necessary if the egg is made with flat ends. The egg should be provided with a pressure gauge, a safety-valve, a 6-inch circular hole with strengthening ring and draw-up manlid, a 1-inch air inlet, the pipe just entering, a 1½-inch or 2-inch outlet pipe, which should reach to within 1½ inches from the bottom of the egg, and a 1-inch drain cock. For the position of the various fittings, reference to Fig. 48 should be made. The egg should be placed below ground, immediately under the finishing tank, and a brick-lined sump should be made under the drain cock as shown in Fig. 48. When setting the egg, a fall of 4 inches in 10 feet towards the drain cock must be allowed. As already mentioned, the tar acids are transferred from the finishing tank to the acid egg by an ever-ready syphon; this piece of apparatus is illustrated in Fig. 47.

The tar acids may be stored in wrought-iron tanks of any convenient shape and size: they should be covered in and a manhole and lid provided. A 1½-inch drain cock of cast-iron should be fitted on the bottom of the tank, and the cock to be used for emptying purposes must be fitted on the side with its centre line 4 inches from the bottom of the tank. It should be a 2-inch cast-iron gland cock. Storage tanks may be supported on brick or concrete piers, at a convenient height for filling barrels. Arrangements should be made for connecting the emptying cock with mains for filling railway tanks or tank boats, also for connecting up to a steam supply in order that an open steam end may be inserted into the tank to steam it out when it requires cleaning.

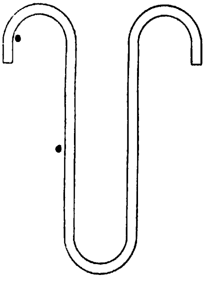

Fig. 47.—Ever-ready Syphon.

In the CO_2 process, one of the most important pieces of apparatus is that from which the supply of carbonic acid gas is drawn. Sometimes the waste gases from the flues of a steam boiler, under which coke is burned, are used, after purifying, for this purpose. This method cannot be recommended. The same may be said of the method of using waste gases from an ammonia distilling apparatus. Undoubtedly the best plan is to employ a special furnace, built just the right size to supply the plant with sufficient purified gas when it is working under full pressure.

There are several patent CO_2 furnaces put on the market by various makers, but it may be preferred to build one's own furnace. Three chief designs of furnace exist: the flat or dead hearth; the firegrate, in which the coke is burned on firebars; and the water-bosh or water-sealed furnace. In the first type of furnace, the fuel is fed to the fire at the top, and in burning it rests on the firebrick bottom of the furnace. A cast-iron door about 18 inches by 10 inches is put in on a level with the bottom of the furnace, on the front of which is an air grid to regulate the admission of air, and through which the clinker is withdrawn. The gas is taken off from the top of the furnace. With this type of furnace, trouble often arises with the air regulation, the fire burns very unevenly, and during the cleaning or clinkering process much unburned coke is withdrawn with the clinker, and the uniformity of the gas is upset for an inordinate length of time. The clinker is often considerable. In the second type of furnace the air regulation is under better control, especially if the ash-pit is closed by a door on the face of which air grids are fitted. The fire burns much more evenly, but unless the bars are water-cooled they are rapidly burned away; even when they are cooled with water, a good deal of trouble is experienced in this direction, and during the removal of the clinker much excess of cold air is admitted to the furnace.

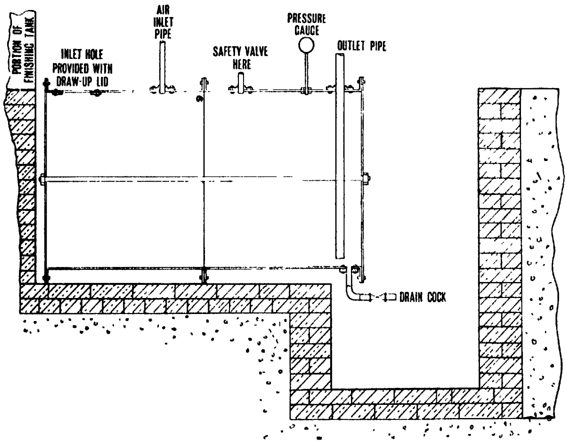

FIG. 48.—Egg for use on Carbolic Plant, etc.

The last type of furnace is, in the writer's opinion, the best. Two furnaces which he designed, and which varied somewhat in detail, both yielded excellent results. They gave very little trouble as regards clinker, and no trouble due to excessive air admission and its resulting uneven quality of gas during cleaning. The fuel is fed in from the top via a hopper and bell valve, and the poking down carried out through poking holes. Ashes, with very little clinker, are removed through the water seal or bosh. The gas is drawn off through a firebrick-lined flue in the side of the furnace near the top. This flue bends round in such a fashion that the position of the exit is at the furnace top, and there it is connected with a cast-iron gas pipe. Air inlets are provided at each of the four sides of the furnace, and they are made so that the quantity of air can be regulated by slides running in frames built in the brickwork. The furnace is lined with best ganister brick; when working properly, the temperature of the furnace is so great as to fuse most, if not all, qualities of firebrick. A staging, supported on brackets, is fitted round the top of the furnace; this is for the man to work upon. The furnace top is also covered with a cast-iron plate. It is advisable to strengthen the furnace with light backstaves and tie-rods. Fig. 49 will show the shape and many details associated with this type of furnace.

As the gas leaves the furnace it carries with it a fair amount of dust, and also impurities such as sulphur dioxide and sulphuretted hydrogen, together with some moisture. These it is necessary to separate as far as possible before the gas enters the reaction tower, or if carbonators are used, these vessels. The dust must be separated first, and then the gaseous impurities, and finally as much of the moisture as possible. A dust separator may be built in the bottom portion of the washing and purifying tower, or erected as a separate piece of apparatus. It should be of cast-iron. A simple and yet efficacious piece of apparatus for carrying out the dust-separating operation is shown with approximate measurements in Fig. 50, and Fig. 51 shows one built in the bottom of a purifying tower. If the dust separator is erected as a separate piece of apparatus, it must be placed between the furnace and purifying tower. In the event of a water-sealed CO_2 generator being used it is a good plan to place the dust separator as near the furnace as possible. The object of this is to keep the separator hot in order to avoid the condensation of moisture, which, if it takes place, will convert the dust into mud. It is necessary to remove frequently the dust from the separator in order to prevent choking.

The purifying or washing tower (Fig. 52) is best constructed of cast-iron sections, square or round in plan. If round, each section should be about 3 feet in diameter, and if square, about 2 feet 6 inches by 2 feet 6 inches. In either case, each section should be 12 inches deep. Each section carries a grid, supported on a ridge cast on the section (see Fig. 52). The grids may be of wood or mild steel; the writer is inclined towards the use of mild steel, as in his experience the amount of corrosion is exceedingly small. Wooden grids eventually become soft and rotten. Mild steel grids should be of ½-inch plate drilled with $\frac{7}{16}$-inch holes at 1-inch pitch. Each grid should be covered with a layer of limestone chips about 1½-inch size, to a depth

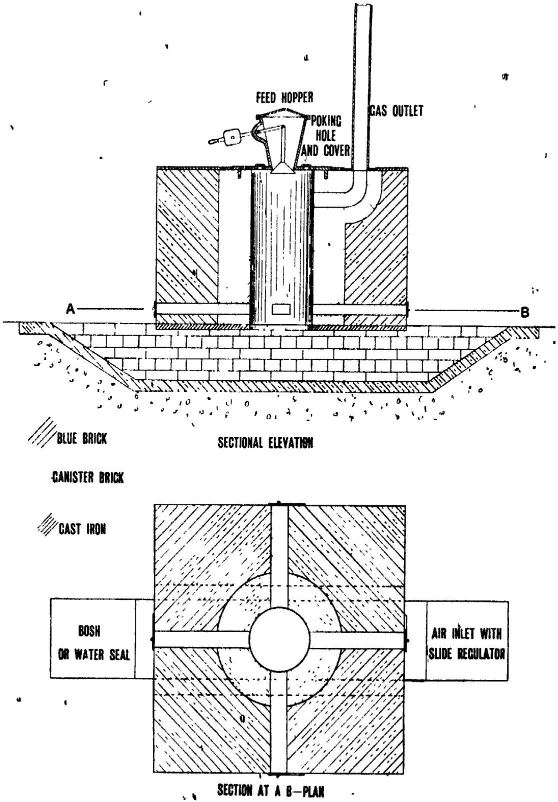

FIG. 49.—Furnace for Generation of CO_2.

between 5 and 6 inches. A hand hole is made in each section, the lower portion of which must be on a level with the top of the grid or tray. The number of sections in the tower will vary according to the quantity of gas passing through it per day.

For a plant burning 800 lbs. of coke per 24 hours, a tower of 8 sections 2 feet 6 inches square will prove quite suitable.

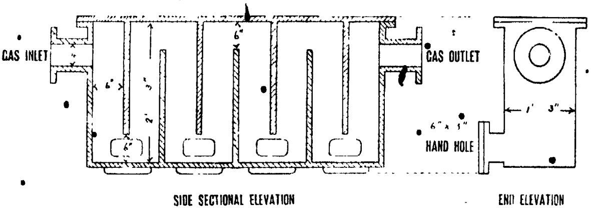

FIG. 50. Dust Separator.

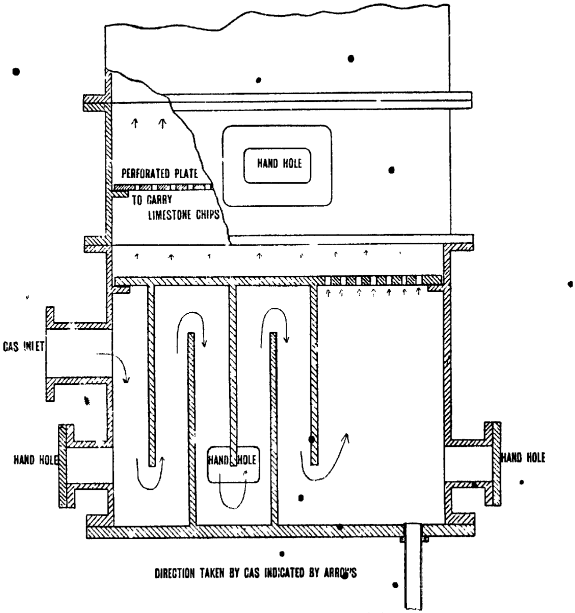

FIG. 51.—Purifying Tower with Dust Separator built in Bottom.

The bottom section has no grid, but should have a hand hole, and into this section the gas enters by a 4-inch cast-iron pipe, the centre line of which is 6 inches from the bottom of the section. A 1-inch or $1\frac{1}{2}$-inch exit for wash water is provided for in the bottom of the section. To the top section is fitted a 4-inch cast-iron gas outlet pipe, and also a 1-inch water inlet. The water is distributed over the top grid by means of a Gurney's jet (Fig. 44). In order that the gas pipes conducting the purified gas from the washing tower can be cleared of any obstruction which may occur—and obstructions have occurred occasionally in the writer's experience—they are fitted with fourway pieces arranged as shown in Fig. 53, the removal of the blank flanges making it easy to shift the obstruction.

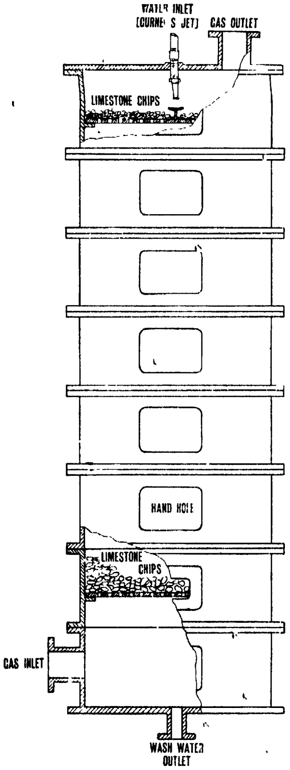

FIG. 52.—Diagram illustrating a Type of Purifying Tower without Dust Separator.

To remove the water which condenses out of the gas (especially in cold weather) and settles in the lowest portion of the gas main, the following simple plan devised by the writer may be used. The gas pipe is allowed a gentle fall until it reaches to within about 14 feet from the point of entry into the carbonating tower, or first carbonating boiler. A flat U-bend is made in the pipe, and in the lower end of this, about the middle, and underneath the pipe, a $\frac{3}{4}$-inch hole is drilled. Into this hole is inserted a cork, into which is fitted a piece of $\frac{1}{4}$-inch bore glass tube, bent as shown in Fig. 53. The depth of the U is made so that it just allows the water in it to resist the pull on the plant without being drawn out of the tube. Immediately any water collects in the gas pipe, it is automatically removed by the glass U-tube without the seal being broken and the admission of air.

In the CO_2 process, the spent liquor, which is really an impure solution of carbonate of soda, is converted into caustic soda by causticising with lime. The pieces of plant required for carrying out this process are: two or three causticisers, two caustic soda tanks, a filter, a pump, and an evaporator. These pieces of plant will be described briefly in the order given.

The causticising tanks are cylindrical and built of wrought-iron or mild steel plates. They may be horizontal or vertical: the latter is the best type to use. Each tank is fitted with a mechanical agitator, an open and closed steam coil, a skimmer pipe, a grid or basket made of bar iron, at the top if of the vertical type, and a gate or treacle valve having a 6-inch opening on the bottom. They should be erected above ground, best on rolled steel joists and stanchions, and above the filter. A water supply should be arranged for over each causticiser.

It is advisable to put in two caustic soda tanks, one for strong caustic soda from the causticisers and the other for weak caustic soda or "weaks"—the washings of the lime mud from the causticisers and the filter. These tanks may be square or rectangular in shape, according to circumstances, and constructed of mild steel plates, the seams being thoroughly caulked. A suction pipe which can be raised and lowered should be fitted to each tank. They should be erected on the floor level, as close to the causticisers as possible.

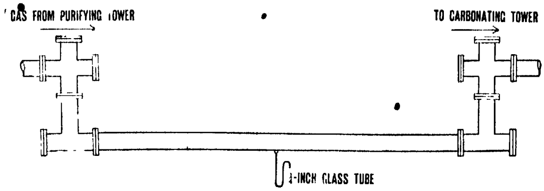

FIG. 53.—U-bend to separate Water from Gas.

The filter is situated immediately under the causticisers, and should be of such a size that it will hold the lime mud from all the causticisers at the same time. It is constructed of mild steel plates, ⅜ inch to 7/16 inch in thickness, and it is best built rectangular in plan. The seams should be double riveted and thoroughly well caulked, and on one side as near the bottom as possible a 2-inch suction pipe should be fitted. Two sets of perforated plates are required: one to form the base of the filter bed and the other to cover the top. These plates are of mild steel, ¼ inch thick, and drilled with ½-inch holes at a pitch of 2 inches. The bottom set of plates are laid on Staffordshire blue bricks at a height of 6 inches, arranged in rows 18 inches apart, on the bottom of the filter. An excellent filter bed is made by using graded granite chips and a top layer of coke breeze, upon which the other set of perforated plates are placed. The thickness of each layer of granite chips and the approximate sizes are as follows: On the bed plates a layer of 1½-inch to 2-inch chips 4 inches deep is placed; then a 3-inch layer of 1½-inch to 1-inch chips; then a 3-inch layer of ½-inch to ¾-inch and then a 3-inch layer of ¼-inch and ⅛-inch chips, above which a 2-inch layer of coke breeze is placed. To dry the lime mud further than is possible with a filter, and to recover the maximum amount of caustic soda in the form of "weaks," the employment of a centrifugal machine is necessary.

Any good pump of the ram type may be connected up to the outlet at the bottom of the filter. The pump should have a 2-inch suction, and the glands on the water end should be packed carefully with "ammonia" packing. This packing is the least attacked by the weak caustic liquor. The pump not only assists in the filtering operation, but pumps the weak caustic liquors, washings, and filtrate, into the evaporator. A connection with the "weaks" tank to the pump suction is made by a by-pass.

If considerable quantities of weak caustic liquor have to be concentrated, then it would be advisable to put in a vacuum evaporator and its appurtenances, using exhaust steam as the heating medium. However, this is seldom necessary in a tar distillery. The usual method is to cover the bottom of a tank of suitable size with a series of coils of 2-inch or 3-inch steam-pipe. A reliable type of steam trap should be fitted on the exhaust end of the coils. To get the best results, the "weaks" should be allowed to stand as long as possible, in order to deposit any lime mud suspended in it. This mud will, if it gets into the evaporator, coat the coils and thus hinder the rate of evaporation. In any case it is as well to clean occasionally the steam coils by scraping them, and then washing down. The evaporator should be erected on rolled steel joists and stanchions for preference, and at a height above the ground level which will permit of the concentrated caustic liquor running into the storage tank by force of gravity. Fig. 54 illustrates diagrammatically one method of arranging a causticising plant.

If it is desired to manufacture 95–97 per cent. cresylic acid, then it is necessary to submit the crude, as it comes from the carbonating tower, to a process of distillation and air blowing. The pieces of plant required to carry out the manufacture of this kind of cresylic acid are as follows: A still charging tank, a mild steel still with a fractionating column, a condenser coil and tank, collecting box, water separator, bottoms receiver, pitch bay, cresylic and carbolic receivers, acid egg and blowing boiler, and foul gas-mains.

It is very convenient to erect the undistilled crude cresylic storage tank at a higher level than the still top and in close proximity thereto. By doing so the still can be charged by force of gravity, and only one passage through the acid egg is necessary; two would be required if the storage tank is placed at a low level. The tank may be of any convenient shape, constructed of mild steel plate, covered in and provided with manhole and lid. An inlet pipe and dipping hole are put into the top, and the outlet pipe for charging the still is placed on the side, its centre line being 4 inches from the bottom. A very convenient diameter for the charge and inlet pipe is 2 inches.

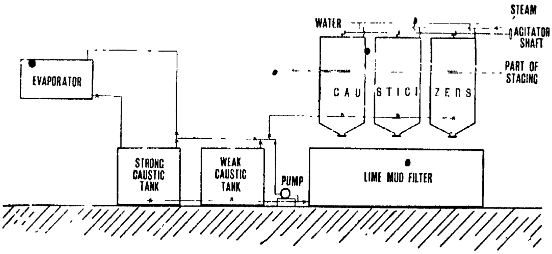

FIG. 54.—Diagram showing One Method of arranging Causticising Plant.

It is advisable to put a 1-inch drain cock in the bottom of the tank, through which any sodium sulphate liquor which separates may be drained away. The separation of the liquor may be expedited by keeping the acid at a temperature of about 70° Fahr. by means of a small steam coil. Every endeavour should be made to keep this liquor out of the still.

A cresylic still is constructed of mild steel plates throughout, and of a similar shape to a tar still. The fittings, such as manhole and lid, charge inlet, swan neck, safety-valve, tail pipe, etc., are also similar to tar still fittings, and the same may be said of the settings, fireplace, flues, etc. The reader is therefore referred to the details given under tar stills in chapters iii and iv.

As a certain amount of carbolic acid is present in the crude cresylic and the value of the former is generally greater than that of the latter, it is advisable to separate these by means of a fractionating column. This piece of apparatus is made of cast-iron and built up of sections of approximately 2 feet in diameter and 9 inches in depth. The size varies somewhat acc the type of column, and the height of it, to a large extent, according to the degree of perfection to which it is desired to conduct the fractionations. A good average number of sections used in a column is fifteen; this includes the top and bottom sections. One of the best types of fractionating column is described and illustrated on pages 134 and 135. The tower is supported on steel stanchions and joists on a convenient portion of the brickwork at the still top. A return pipe is fitted into the underneath portion of the bottom section of the tower and inserted into the still top, a U-bend being made in the pipe to act as a seal. The bottom section is also connected to the swan neck of the still, and an arrangement is made for by-passing the tower, so that during the water and cresylic stages the vapours can be conducted direct to the condensing worm. These various details are illustrated diagrammatically in Fig. 55. It is a good plan to arrange that all the sections can be drained after each operation.

The condenser coil and tank are similar to those used with tar stills (see page 51) and so is the collecting box (see page 51). For the separation of the water and tar acids as they run into the collecting box, this piece of apparatus is connected to a separator of the same kind as that described on page 53, but it is arranged for the water to be removed from the top of the separator and the tar acids from the bottom.

After a certain portion of the contents of the still have been worked off, the residue is allowed to cool a little and then run into a tank, known as a "bottoms" receiver, to be worked up with the "bottoms" from other operations when a sufficient quantity has accumulated. A horizontal boiler tank makes an excellent receiver. It is set below the still run off or tail pipe, and is connected up to the same. Connection is also made with a pump, or it is arranged that the receiver can be tightly closed and then emptied by air pressure. In this case it is connected to an air compressor, and an outlet tube is fitted so that it reaches to within about 2 inches from the bottom. As the "bottoms" become viscous, it is advisable to put in a closed steam coil of one lap, built of 1-inch wrought-iron pipe, in order to warm them up prior to charging them into the still. The receiver should have a manhole and lid of the usual size.

The "bottoms" are finally worked to pitch, and the pitch is either run off and mixed with a big batch of pitch from the tar stills, or else run into a special bay. If a special bay is desired, it is constructed in a similar manner to the large bays described on page 60, but is of course much smaller. A 4-inch pipe is connected to the tail pipe of the still for running off the pitch, and by means of a reducing T-piece, and the necessary cocks, the "bottoms" pipe, which is 2 inches in diameter, is connected to the pitch pipe.

Receivers for the cresylic and carbolic acid may be constructed of mild steel, and square, rectangular, or cylindrical in shape. If cylindrical, they may be horizontal or vertical, and it is a good plan to arrange so that the contents can be transferred by air pressure to storage or mixing tanks, in the case of carbolic, and to an air blowing boiler for purification in the case of cresylic. Square or rectangular tanks are not suitable, if it is desired to remove their contents by air pressure, and so will have to be connected up to a pump or egg.

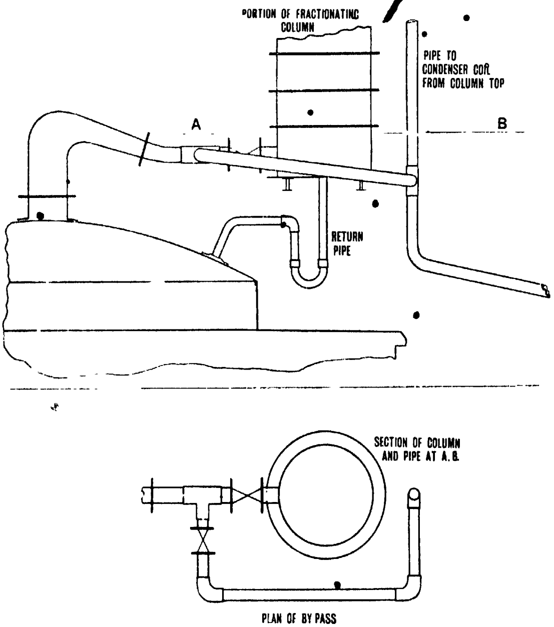
PORTION OF FRACTIONATING COLUMN
PIPE TO CONDENSER COIL FROM COLUMN TOP
A
B
RETURN PIPE
SECTION OF COLUMN AND PIPE AT A.B.
PLAN OF BY PASS

Fig. 55.—Diagram illustrating a Method of attaching Fractionating Column to a Cresylic Still and arranging a By-pass.

Cresylic acid from the still generally contains sulphuretted hydrogen and other sulphur compounds in sufficient quantity to render it foul in smell. It is necessary to sweeten the acid before despatching to customers, and this process is carried out in a large cylindrical boiler tank, placed in a horizontal position.

Along the bottom of this tank is fitted a perforated coil of 1-inch wrought-iron tubing, through which air is passed during the operation. The top of the tank is connected to a 2-inch foul gas main, which, in its turn, is connected with a purifier or a seal pot and ejector. In the latter case the gas is burned underneath the steam boilers, and the ejector may be employed to draw air through the cresylic acid in the tank by leaving an open end on the upright length of the coil, just a little above the point at which it enters the boiler. The foul gas may of course be drawn through the purifier by an ejector and the same method of air-blowing the cresylic employed. If an ejector is not used, it is necessary to connect the perforated air coil to an air compressor. It is as well to provide this tank with a manhole and lid of the usual dimensions. An inlet pipe is also required, and so is an outlet pipe, with cast-iron cock, through which barrels are filled. A by-pass should be connected to the outlet, so that when it is desired to load the acid into a railway tank wagon, it can be run into an egg, and then filled into the wagon by means of air pressure. A suitable kind of egg has already been described on page 96.

In connection with the recovery of tar acids, the Hird continuous tar acid extraction plant, and also Peppers' patent extractor, which is manufactured by W. C. Holmes & Co., Ltd., are worthy of notice.

The Hird plant is illustrated diagrammatically in Fig. 56, and the method of working is as follows: The apparatus is so arranged that the correct quantity of caustic soda lye for the removal of the tar acids from a given quantity of oil is automatically apportioned. In the event of the flow of oil to be washed varying during its passage through the plant, then the quantity of caustic soda lye is automatically adjusted to meet that variation. On reference to Fig. 56 it will be noticed that on the top of the plant are two tanks, one containing caustic soda at a fixed level and the other unwashed oil, which is supplied from the usual oil-storage tank.

In the event of the flow of unwashed oil varying, the level in the tank will rise or fall. This rise or fall is communicated to an equilibrium lever by means of a float which depresses or raises a cast-iron slot-dipping pipe into the caustic soda lye; with more or less flow the dipping slot would be lower or higher and would consequently allow a larger or smaller quantity of lye to flow into the downtake tube.

The oil and caustic soda lye mix together in the manner shown in the figure and then flow downwards into an upward flow mixing tube. At the bottom of this tube is a perforated steam-pipe which is connected to a steam inlet pipe. Upon this pipe is fitted an aspirator, which, during the passage of the steam, draws air from the atmosphere. This, along with the steam, brings about a thorough mixing of the caustic soda lye

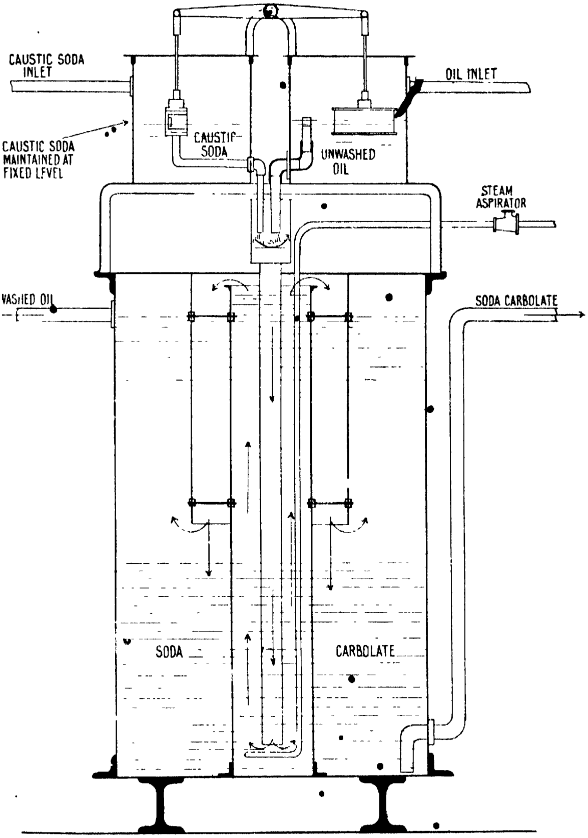

FIG. 56.—Diagram of Hird's Patent Continuous Phenol Extraction Plant.

and unwashed oil in the tube. The mixture then overflows at the top of the tube, and continues a downward course to a circular baffle as shown in the figure. By this time the whole of the tar acids have been extracted from the oil, and as the mixture leaves the baffle the washed oil rises to the upper portion of the tank and the carbolate sinks to the bottom.

The washed oil leaves by a pipe fitted at the top of the tank and the carbolate by a pipe the outlet of which is near the bottom of the tank, and which rises vertically outside to the same height as the washed oil outlet. The depth of the carbolate in the tank is automatically controlled by means of the automatic feed, and it is possible to vary this so that, if necessary, the carbolate can be raised or lowered in the main tank.

Peppers' patent extractor is illustrated in Fig. 57. For the satisfactory manipulation of this plant two tanks are required to hold caustic soda lye of different strengths and one tank to hold unwashed oil. There are two mixing chambers and separation tanks, one for the extraction of crude carbolic and the other for crude cresylic. Before the extraction process is commenced the oil and caustic soda lye are heated to a suitable temperature, approximately 80° Fahr., by means of a dry steam coil in the bottom of each tank. The strength of the caustic soda lyes will depend upon whether the tar acids are to be recovered by the CO_2 process or by the sulphuric acid method. In the case of the former they may be approximately 1.115 specific gravity for carbolic and 1.125 for cresylic, and of the latter 1.125 for carbolic and 1.225 for cresylic.

Unwashed oil from the storage tank and caustic soda lye of the determined strength for the extraction of crude carbolic acid are run into the conical shaped device at the mouth of the mixing chamber A, which, as will be seen on inspecting the diagram, Fig. 57, is fitted with a series of sectional plates. The flow of oil and lye is controlled by the cocks B and C.

On leaving the conical mouthpiece the two liquids enter into section 1, which consists of a plate with slotted holes at the side, and they splash on this plate and run through the slots into section 2, which consists of a plate with a centrally fixed hole to lead the oil and soda into section 3, which is similar to section 1. This process of agitation continues until the mixture of oil and soda has passed through the whole six sections. On leaving the mixing chamber A the two liquids enter the small tank D, in which separation takes place.

The separated carbolate passes through a small space at the bottom of the curtain plate E, and then through the cock F, on its way to the carbolate stock tank, to await further treatment.

The partly washed oil flows through the regulating cock G, and is led into the second mixing chamber H, along with caustic soda lye from the storage tank containing that of the correct strength for the recovery of crude cresylic acid.

The second mixing chamber is of slightly different construction to the first, but is practically on the same principle. It consists of a conical-shaped mouth, like the one in the first chamber, and flat plates with centrally fixed holes to which are fitted small neck pipes on the bottom sides, also three shallow dished pans with slotted openings round the edge. These dished pans are placed between the plates.

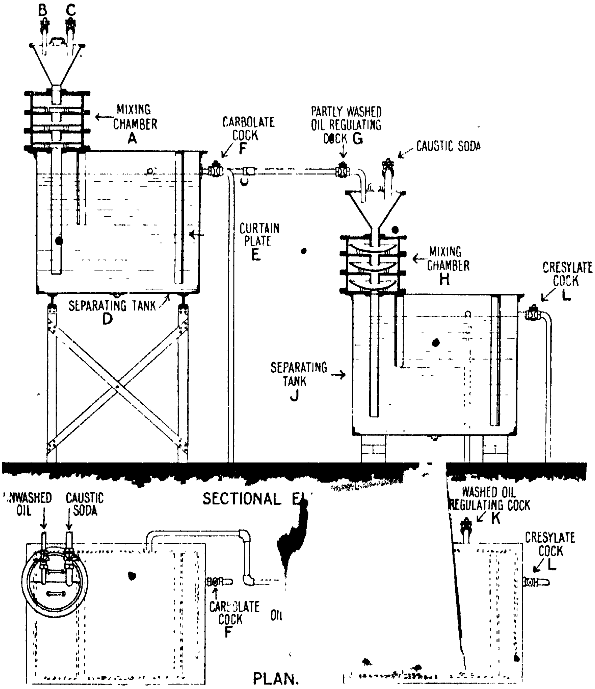

FIG. 57.—Peppers' Patent Continuous Extractor for the Recovery of Carbolic and Cresylic Acids.

The liquids on entering section 1 pass through the central hole into the dished pan beneath it, flowing through the opening at the edge on to section 2, where they splash together and run through the central hole into the dished pan, as in section 1.

This goes on through all the sections. On leaving the last section the mixture enters the tank J, which is similar in construction to tank D on the crude carbolic portion of the plant. The separation of the oil and cresylate takes place in this tank, the oil flowing through the regulation cock K, and the cresylate under the curtain plate and through the cock L, into their respective storage tanks.

CHAPTER VIII

THE RECOVERY OF CARBOLIC AND CRESYLIC ACIDS

Crude carbolic and cresylic acids—chemical and physical properties of phenol and the cresols—causticising soda ash and "spent liquor"—washing oils for tar acids—interchange process—particulars relative to washing oils for crude carbolic and cresylic acids—works costs—recovery of tar acids from phenolate—sulphuric acid process—CO_2 process—distillation of "sprung" cresylic acid—air-blowing distilled cresylic acid

CRUDE carbolic and cresylic acids are a source of considerable income to the tar distiller, and in all well regulated works every care is exercised to recover the maximum amount of each from the tar distillates in which they exist. These two articles consist of mixtures of phenols, chiefly of the monohydric series, of which phenol, carbolic acid or hydroxybenzene ($C_6H_5.OH$) is the first. The next in the series are the three isomeric cresols or hydroxytoluenes ($C_6H_4CH_3.OH$).

Phenol occurs in the form of colourless deliquescent prisms which melt at a temperature of 42.5° C., and turn pink on exposure to light. It boils at 183° C., and can be distilled in a current of steam. At 0° C. phenol possesses a specific gravity of 1.084, at 18° C. 1.065, and at 33° C., 1.0597. In ether, alcohol, carbon disulphide, benzene, carbon tetrachloride, tetrachlorethane, glacial acetic acid and glycerine, phenol is soluble in all proportions. It is also soluble in the fixed and volatile oils. A mixture of half camphor and half phenol crystals liquefies on standing, with a fall in temperature. On account of the high molecular depression of phenol and the small molecular weight of water a small percentage of the latter (about 8) renders phenol liquid at ordinary temperatures. It is only sparingly soluble in water, 1 part dissolving in 15 parts of water at 16° C. Aqueous and alcoholic solutions of phenol give a violet colouration with ferric chloride. Phenol is used largely in the manufacture of salicylic acid, salol, picric acid, phenacetin, and many other important substances.

The three isomeric cresols, ortho, meta, and para, occur in commercial cresol or cresylic acid, the proportion of each varying in different samples. Schulze gives the following average figures: M. cresol, 40 per cent.; O. cresol, 35 per cent.;

and P. cresol, 25 per cent. In water the three cresols are only slightly soluble. At 15° C. 100 parts of water dissolves 2.5 parts of the ortho, 0.53 parts of the meta, and 1.8 parts of the para. Alcohol and ether dissolve the three isomers with ease.

TABLE XVI

	O. [1 2] Cresol.	M. [1 3] Cresol	P [1 4] Cresol.
M. Pt. (corrected)	30° C.	3°–4° C.	36° C.
B. Pt. (corrected)	190.8° C.	202.8°	201.8° C.
Sp. gr.	1.0053 at 65° C.	1.0498 at 0° C.	0.9962 at 66° C.

Owing to the presence of the C_6H_5 radicle in phenol the OH group (hydroxyl) possesses weak acid properties (its basic character being somewhat modified). This is shown in its behaviour with caustic alkalies, with which it reacts to form phenolates. One of these which is of importance to the tar distiller is known as sodium phenate, and it is formed by acting upon phenol with caustic soda. It is represented by the formula $C_6H_5.ONa$, and the reaction is indicated by the following equation :—

$$C_6H_5.OH + NaOH = C_6H_5.ONa + H_2O.$$

The hydroxyl (OH) group in the cresols is also weakly acidic in property, but not so strong as in the case of phenol. This is probably due to the modifying influence of the CH_3 group in the $C_6H_4.CH_3$ radicle. By acting upon the cresols with caustic soda, cresylates are formed having the formula $C_6H_4CH_3.ONa$. If a mixture of phenol and cresols is treated with insufficient caustic soda to combine with the whole, then a preference is shown for the phenol owing to its stronger acidic property. This fact is used in practice in the recovery of carbolic acid from oils which contain both phenol and cresols. Sodium phenolate and the sodium cresylates are stable in aqueous solution, but are readily decomposed by solutions of mineral acids, hydrochloric acid gas, sulphur dioxide, and carbon dioxide.

In the process of recovering tar acids from the distillates which contain them, a solution of caustic soda is used, the strength of which varies somewhat according to the kind of acid to be extracted or the process employed. The caustic soda is sometimes made at the tar works and concentrated by evaporation, and in those works employing the CO_2 process, the manufacture of caustic soda (causticising of the spent liquors) is an everyday occurrence. On this account a description of the process of causticising soda ash and spent liquors will be given, before dealing with the recovery processes.

The best quality of soda ash (sodium carbonate) to use is that known as 58 per cent. alkali. This contains on an average 98.75 per cent. of actual sodium carbonate (Na_2CO_3). In the process of converting this material into caustic soda (technically, causticising) quicklime of a high grade is employed; the best lime for the purpose is white Buxton lime. Theoretically the reaction which takes place is shown by the following equation:—

$$\underset{106}{Na_2CO_3} + \underset{74(56CaO)}{Ca(OH)_2} = \underset{80}{2NaOH} + \underset{100}{CaCO_3}$$

In practice it is necessary to use between 10 and 15 per cent. of lime above the theoretical quantity, as the reaction is a reversible one, and, to obtain the best results, the soda-ash solution must be as dilute as possible. Using an ash solution of 20–22° Tw. (1.10–1.11 sp. gr.), the amount of sodium carbonate causticised will be between 95 and 97 per cent. Some prefer to add slaked lime to the ash solution, but in the writer's opinion it is far better to employ quicklime and make use of the heat generated during its hydration to assist in the causticising of the sodium carbonate.

The process is carried out as follows: Water is run into the causticiser until it reaches within a few inches of the bottom of the lime grid. Open steam is turned on as soon as the coil is well covered, and steam is allowed to pass during the remainder of the time of charging, and until the water practically reaches its boiling-point. The desired amount of soda ash is added to the water, commencing as soon as signs of ebullition appear, care being taken not to add more ash than is necessary to give a specific gravity of 1.11 (22° Tw.) at 60° Fahr. It is an easy matter to calculate this amount for any size of causticiser, once and for all, from the figures obtained by carrying out a small experiment in the chemical laboratory. The ash solution should cover the bottom bars of the grid about one inch, and while at a temperature of about 198° Fahr. the lumps of caustic lime should be thrown into the grid, a few shovelfuls at a time, until the calculated quantity has been added. Let each lot of lime "break down" and wash out of the grid before adding a further quantity. Keep the agitator running slowly all the time. For a causticiser containing about 1200 gallons the operation should take about 15 to 20 minutes. As soon as all the lime is in, shut off the open steam, put on the closed steam, and increase the speed of the mechanical agitator a little.

After about 1½ hours it is as well to remove a sample and test it to see how the causticisation is progressing. It generally takes about 1½ to 2 hours after the lime is all in to complete the operation. This time may be shortened a little if a large excess of lime is used, for instance 110 lbs. of lime to every 100 lbs. of soda ash used.

When the causticisation is complete, the contents of the causticisers are allowed to remain at rest for about 3 hours, and then the clear caustic soda removed by a skimmer pipe to the storage tank; as much as possible of the caustic soda solution should be run off. To the mud is now added some cold water, the volume depending upon the quantity of mud; if 10 cwts. of soda ash have been causticised, then about 250 gallons of water will be sufficient. Open steam is turned on and the agitator started, and both the passage of steam and the agitation are continued until the contents of the tank begin to boil. One hour is allowed for settling, and then the clear liquor is run direct to the evaporator, any milky liquor being passed through the filter first. A further 250 gallons of cold water are added to the mud, and well mixed in by mechanical agitation only, after which about one hour is allowed for settling, the clear liquor is skimmed off for evaporation, and the soft mud then run on to the filter. The liquid which filters through is evaporated down, and then added to the strong caustic soda with the other concentrated washings. By this method of washing it is possible to reduce the content of actual caustic soda ($NaOH$) to 0.5 per cent. If it is desired to dry the mud further, it may be transferred from the filter to a special centrifugal machine.

Before causticising the "spent liquor," which is separated from the tar acids at the divider tanks, it is necessary to bring it up to a standard strength by adding soda ash. The quantity of ash it is necessary to add is found by submitting a sample of the spent liquor to analysis. A good standard to work to is 10 grams of ash per 100 c.c.'s. The amount of ash required to bring the "spent liquor" up to strength being added, causticisation and the washing of the lime mud are carried out in a similar manner to that just described. With reference to the amount of lime to be added, the writer has obtained the best results by using 6 to 6½ cwts. of best Buxton lime for every 10 cwts. of actual soda ash in solution in the "spent liquor." It is not possible to gauge the strength of the "spent liquor" by means of a hydrometer, as it contains impurities which affect the specific gravity. Caustic soda for washing out cresylic acid is often made a little stronger, and this necessitates reinforcing the causticised "spent liquor" by the addition of some strong caustic soda solution, or by evaporation, this latter operation naturally raising the content of caustic soda by reducing the quantity of water. Unfortunately, evaporation increases the percentage of impurities, and if this gets large the reaction between the tar acids contained in an oil and the caustic soda in the liquor is somewhat retarded.

Crude carbolic and cresylic acids are extracted from crude naphtha, light oil, carbolic oil, or light creosote. The methods of dealing with these distillates before extracting the tar acids vary more or less in different works. Sometimes the oils are submitted to distillation first, separating into two or three fractions; at other times a portion of the tar acids is washed out of the oils, after which they are distilled and the distillates washed for tar acids. Circumstances determine which process is carried out and also the number of fractions made, and their cut points. Whichever process is used the tar acids are washed out with caustic soda lye, and recovered by either the CO_2 or sulphuric acid method.

Before the oils are washed with the caustic soda lye they should be allowed to settle in the washer for a short time in order to settle out any entangled ammonia water. This material will not only dilute the lye, but as it generally contains ammonium sulphide a reaction will take place, resulting in the formation of sodium sulphide and ammonium hydrate; the former compound is incapable of combining with tar acids, and thus reduces the active strength of the lye. During the settling out process, any oil which separates naphthalene ("salts out") must be kept warm by means of a closed steam coil, and it is also necessary to wash this type of oil at an elevated temperature. This temperature must not be too high, and if the caustic lye is used hot the same precaution must be taken. If the oil or lye is too hot the amount of tar acids extracted is not so great as when warm or cold. Also, if the process of interchange is being carried out and the carbolate or oil is too hot there is a tendency for the carbolate to give up some of its tar acids to the oil. A good "average" temperature to use when washing is 85° Fahr. It should be borne in mind that the caustic soda lye must not be too strong.

The method of interchange is employed in both the CO_2 and sulphuric acid processes. It consists in adding a phenolate containing a little carbolic and much cresylic acid, or all cresylic acid, to an oil rich in carbolic acid, when the carbolic acid in the oil displaces the cresylic acid in combination with the soda in the phenolate, the cresylic acid going into solution in the oil. Interchange takes place.

If the tar acids are to be recovered by the sulphuric acid process, the fresh, or "clean," caustic soda lye used for the purpose of washing an oil is moderately strong, varying in specific gravity from 1.150 to 1.225 at 60° Fahr. The specific gravity of "clean" lye used in the CO_2 process varies between 1.110 and 1.140, but that from "spent liquor" generally has a much higher specific gravity (at times 1.150), due to impurities in solution. Sometimes "clean" lye is used to wash a fresh oil, and with reference to the amount of caustic lye required, this will vary according to whether it is desired to take out the whole of the tar acids or only a portion. By testing the oil for its content of tar acids, and using the equation given on page 114, or by adding measured volumes of lye to a known quantity of oil until no further decrease in bulk takes place, the chemist can determine approximately how much lye to use.

In following through an interchange process, using moderately strong lye at the finish, it will be assumed that the phenolate with which it is desired to wash the fresh oil stands at a specific gravity of 1.110 and contains 21 per cent. of tar acids possessing a crystallising point of 60° Fahr.

It is not possible to give detailed figures with reference to the amount of phenolate to be put on an oil; this will vary according to the quantity of oil it is required to wash and also with the kind of oil. The amount must, therefore, be determined by experiment in the chemical laboratory. After the oil has been washed with the phenolate containing 21 per cent. of tar acids, it is allowed to settle for a short time, say about half an hour; the phenolate is then run off to a storage tank, tested, and retained for further use. The oil is then washed with another phenolate containing, say, tar acids of a crystallising point of about 58° Fahr. With a good oil the crystallising point of the tar acids in this phenolate will be probably raised to about 60° Fahr. A further settling of the oil and phenolate is allowed to take place and the phenolate removed to a storage tank, or if desired into the tank containing the phenolate which has in solution the higher crystallising acids. The oil may now be washed with another phenolate containing tar acids possessing a crystallising point of, say, 45° or 50° Fahr. The crystallising point of these acids will probably be increased to 50° or 55° Fahr. A settling is allowed, as already described, and the phenolate removed. Sometimes the oil is now washed with a strong solution of caustic soda, the specific gravity of which may be 1.175 at 60° Fahr. The resulting phenolate is, as a rule, used on a fresh oil. Should the oil be particularly rich in crystallisable acids, a further wash with phenolate may be given before using caustic soda lye; and in this connection it should be urged that tests be made in the chemical laboratory throughout the whole operation of washing.

The following particulars relative to washing oils for crude carbolic only or for crude carbolic and crude cresylic will no doubt prove useful to the student. They are taken from actual works practice.

Crude Naphtha.—Washed free of tar acids (total extraction): 1000 gallons of oil taken.

350 to 450 gallons of caustic soda lye at 22° Tw., or equivalent in active strength, if for CO_2 recovery process, or at 30–35° Tw. if for sulphuric acid recovery process. Resulting phenolate reserved for interchange.

Light Oil.—Washing for carbolic only (*a*): 3000 gallons of virgin oil taken.

1st wash.—1000 gallons caustic soda lye (7.6 grams NaOH in 100 c.c.). Resulting phenolate sent direct to CO_2 carbolic recovery plant.

2nd wash. 600 gallons caustic soda lye (7.6 grams NaOH to 100 c.c.). Resulting phenolate sent direct to CO_2 recovery plant.

3rd wash. 1000 gallons weak phenolate off once distilled light oil or off crude naphtha or virgin light oil.

Test resulting phenolate. If phenols low in crystallising point use for interchange on light creosote, if crystallising point suitable run phenolate to recovery plant.

4th wash. 1000 gallons weak phenolate.

Resulting phenolate to be used for interchange.

After the four washes distil the light oil. The distillate, known as "once distilled light oil," is washed with clean caustic soda lye until free from tar acids, and the resulting phenolate is kept for interchange purposes.

2000 gallons once distilled light oil for washing.

1000 to 1500 gallons caustic soda lye added according to the amount of tar acids present.

Note.—If using the sulphuric acid recovery process the caustic soda lyes are used stronger and correspondingly less in volume.

Light Oil.—Washing for carbolic only (*b*): 3000 gallons of virgin oil taken.

1st wash. 1000 gallons weak phenolate off light oil, crude naphtha or once distilled light oil.

Resulting phenolate reserved for interchange.

2nd wash. 1600 gallons weak phenolate as used for 1st wash. Resulting phenolate to be used for interchange, say, on light creosote (or carbolic oil).

Note.—After this wash treat the light oil as in example (*a*) above.

Light Oil.—Washing for carbolic and cresylic (*a*): 3000 gallons of virgin oil taken.

1st wash. 1000 gallons of caustic soda lye containing 7.6 grams NaOH in 100 c.c.

Resulting phenolate sent direct to CO_2 carbolic recovery plant.

2nd wash. 600 gallons caustic soda lye (7.6 grams NaOH to 100 c.c.).

Resulting phenolate sent direct to CO_2 carbolic recovery plant.

3rd wash. 1000 gallons moderately weak phenolate from interchange carbolate boiler.

Resulting phenolate if crystallising point of tar acids suitable sent to carbolic recovery plant, if crystallising point still too low use for interchange again.

4th wash.} Each of 1000 gallons caustic soda lye at 30° Tw.
5th wash.} Resulting phenolate sent to cresylic recovery plant (CO_2 process).

Notes.—(*a*) Some distillers prefer to send the light oil to the still with about 4 per cent. to 6 per cent. tar acids left in, and then wash the once distilled light oil as already described. (*b*) If the sulphuric acid recovery process is used the clean caustic soda lye may stand at 35–40° Tw., and correspondingly less in volume is required.

Light Oil. Washing for carbolic and cresylic (*b*): 3000 gallons virgin oil taken.

1st wash. 800 gallons caustic soda lye (7.6 grams NaOH to 100 c.c.).

Resulting phenolate sent to CO_2 recovery plant or to interchange phenolate boiler according to crystallising point of tar acids.

2nd wash. 800 gallons caustic soda lye (7.6 grams NaOH to 100 c.c.).

Resulting phenolate dealt with as that from 1st wash.

3rd wash.} Each 1000 gallons caustic soda lye at 30° Tw.
4th wash.} Resulting phenolate sent to cresylic recovery plant (CO_2 process).

Note (*a*).—Test oil and if not free of tar acids put on more caustic soda lye according to requirements.

Notes (*b*) and (*c*)—See notes (*a*) and (*b*) under light oil washing for carbolic and cresylic (*b*) above.

Middle Oil.—Washing for carbolic only: 3000 gallons oil taken.

1st wash. 1000 gallons caustic soda lye (7.6 grams NaOH to 100 c.c.).

Resulting phenolate sent to CO_2 carbolic recovery plant.

2nd wash. 500 gallons caustic soda lye (7.6 grams NaOH to 100 c.c.).

Resulting phenolate sent to carbolic recovery plant (CO_2 process), or 800 gallons caustic soda lye (strength as above).

Resulting phenolate reserved for interchange on light oil.

Middle Oil.—Washing for carbolic and cresylic acid: 3000 gallons oil taken.

1st wash. 1000 gallons caustic soda lye at 7.6 grams NaOH to 100 c.c.

Resulting phenolate sent direct to carbolic recovery plant.

2nd wash. 1000 gallons caustic soda lye, strength as in 1st. wash.

Resulting phenolate used for interchange on light oil, and then sent to carbolic recovery plant (CO_2 process).

3rd wash. 1100 gallons caustic soda lye at 30° Tw.

Resulting phenolate sent to cresylic recovery plant, CO_2 process.

4th wash. 1100 gallons caustic soda lye at 30° Tw.

Resulting phenolate sent to cresylic recovery plant (CO_2 process).

Note (*a*).—Test oil to see if it requires any more caustic soda lye.

Note (*b*). If the sulphuric acid recovery process is used, lye of 35° Tw. may be used for the carbolic extraction, and 45° Tw. for the cresylic acid extraction, and a less volume will be required in each case.

With reference to manufacturing costs it is not possible to give any but average figures, as the cost of raw materials and labour vary from time to time, and in different parts of the country. The average cost for labour and chemicals to produce 1 gallon of 60° crude carbolic acid by the CO_2 process is 1.62d., and if carbolic and cresylic CO_2 recovery plants are worked together the average cost for labour and chemicals to produce 1 gallon of 60° carbolic is 1.48d., and 1 gallon of 97–99 per cent. cresylic, 1.60d. The cost of producing 1 gallon of tar acids by the sulphuric acid recovery process averages out at about 4d., this high figure being due to the fact that all the caustic soda. is wasted, and a larger volume of B.O.V. is required than in the CO_2 process.

Table XVII gives the results of some works experiments on washing oils which may prove useful to students.

In all the washing processes care must be taken not to agitate too vigorously or too long, as there is a possibility, if this is done, of forming undesirable emulsions which may take several hours to separate. Some of the lighter tar distillates, such as crude naphtha, once run light oil, and sometimes even virgin light oil are washed entirely free of phenolic bodies, and there are cases when even a light creosote is served in the same way. At times, however, virgin light oil and light creosote are only partially washed for tar acids and then submitted to a distillation. It is sometimes preferred to distil the light oil and light creosote previously to washing for tar acids. Which of these various methods is used will depend entirely upon the circumstances existing in the works. It should be remembered that an oil containing a fair amount of naphthalene will deposit that substance in the washer very freely after the tar acids have been washed out.

TABLE XVII

Oil	T A.	Wash.	Carbolic		Caustic soda lye (7.6 grams NaOH per 100 cc.).
			Water	Cryst pt.	
	Per Cent		Per Cent.	Fahr.	Gallons.
Light oil,	27½	..	..	..	..
3000 galls.	22	1st	14.5	76°	1000
	18½	2nd	12.5	67°	600
	15	3rd	13.0	60.5°	600
	12	4th	15.0	47.5°	500
	9½	5th	15.0	32.0°	200
Crude naphtha,	6	..	..	..	..
1000 galls.	0	1st	14	39.5°	400
Middle oil,	20	..	..	..	..
3000 galls.	15	1st	14	64°	800
	12	2nd	13.5	55°	350
Re-distilled light	22	..	..	..	..
oil, 1550 galls.	16	1st	14	not at 28°	400

It appears that tar acids assist in keeping naphthalene in solution. It is necessary then, in cases of this description, to keep the oils at a temperature above that at which the naphthalene contained therein will crystallise out. As the majority of tar distillers manufacture crude carbolic and cresylic acids, it is necessary to run those phenolates which contain tar acids which do not crystallise at, say, about 35° Fahr. into special tanks to be worked up for cresylic acid. Only those phenolates which contain crystallisable tar acids are used for the manufacture of crude carbolic. The last wash off the light oils, and generally all the washes but the first off light creosotes, are used for the manufacture of cresylic acid.

The next process is to recover the tar acids from the phenolate, nd the method used is the same whether the phenolate conains crystallisable acids or cresylic acid.

Dealing with the sulphuric acid "springing" process, which enerally follows the interchange process just described, the henolate is run into a suitable tank and diluted with water until s specific gravity reaches 1.08 at 60° Fahr. It is then allowed o rest for an hour or two, in order to allow any oil which may e held in suspension in the phenolate to rise to the surface. his oil is skimmed off, as should it get mixed up with the crytallisable acids it will reduce the crystallising point, or, on the ther hand, should the acids be non-crystallisable (cresylic cid), it will probably bring down their value by increasing the mount of impurity in the finished product.

After the oil is skimmed off, sulphuric acid of about 146° w. (B.O.V.) is added carefully, with thorough stirring. The mount of acid necessary to "spring" the tar acids should not e exceeded, and can be found by occasionally testing the ontents of the "springing" tank with blue litmus paper. Vhen the contents are just acid to litmus, after a thorough gitation, they are allowed to rest for from six to eight hours. he tar acids are then separated from the sodium sulphate quor underneath by first of all removing the latter through bottom drain cock, care being taken that no tar acid escapes uring the operation. The sulphate liquor is run to the sewer. Vhen tar acids begin to show, it is as well to allow a further ettling of about ten minutes or so, or to run a few gallons hrough a separator. The tar acids may then be conducted to storage tank, and tested for strength, prior to mixing with ther strengths, or to filling into packages for despatch.

With reference to the strength of the sulphuric acid used, he writer prefers to dilute the B.O.V. to about 110° Tw. and to eep the phenolate at a specific gravity of 1.10 at 60° Fahr. f too strong an acid is used to "spring" the phenolate, there s a risk of the sodium sulphate crystallising out in the "springng" tank during the settling period, and if this takes place, it vill make it very awkward when the time comes to carry out he separating operation. Strong acid is also liable to act upon he phenols, forming sulphonic acids: these bodies being unlesirable in either crude carbolic or cresylic, as they split up luring the refining operation when the material is distilled. The tar acids should be allowed to rest in the storage tanks ome two or three days, in order to settle out any entangled ulphate of soda liquor. This is necessary in the case of both arbolic acid and cresylic acid.

It is desirable to clear the storage tanks occasionally of he soda sulphate liquor and sometimes crystals which settle at he bottom. Should crystals form, it is as well to steam the tanks out by inserting a temporary 1-inch steam main into the tank.

Carbolic acid is sold in various qualities, such as 40's, 45's, 50's, 60's, etc., and it is possible by a process of mixing to build up any desired quality, either from the phenolates or the "sprung" carbolic acid. A very simple calculation will give the approximate volume required. The mode of calculation as used on "sprung" acid is shown in the following example: Suppose in one storage tank there are 200 gallons of 55's carbolic and in another tank a quantity of 45's acid. It is required to convert the 55's into 50's carbolic; then—

$$\begin{aligned} 200 \times 55 + x45 &= 50\,(200 + x) \\ x(45 - 50) &= 200\,(50 - 55) \\ \therefore -x5 &= -1{,}000 \\ x &= \frac{1{,}000}{5} = 200 \text{ gallons of 45's acid are required.} \end{aligned}$$

In the CO_2 process the oils are washed with a caustic soda lye of a strength sufficient to absorb, in the case of carbolic acid, an amount which, when the phenolate is tested, will correspond to about 15 per cent. of the phenolate, and in the case of cresylic acid about 20 per cent. The caustic soda as obtained from the causticisers, if the process is carried out properly (see page 115), will be of sufficient strength to yield a phenolate containing 15 per cent. approximately of tar acids, and, as already mentioned on page 116, if the lye is to be used for the recovery of cresylic acid, it must be reinforced with a little strong caustic soda made with the 77 per cent. solid caustic soda or with the electrolytic liquid. The interchange method may be used in the CO_2 process of recovery, but a little more care is necessary in carrying it out.

Before washing the oils, it is absolutely essential to allow any ammonia water to settle out. This is necessary, as it not only reduces the percentage of active agent (caustic soda) in the lye by dilution, but also by combination with the sulphur which exists in the ammonia water as ammonium sulphide, sodium sulphide being formed. It appears, from the results of a number of experiments made by the writer and others, that part of this sodium sulphide is converted into sodium sulphate during the progress of the phenolate through the plant.

In the process under consideration, the phenolate is "sprung," or, decomposed, by carbon dioxide (CO_2), which is contained in the gas prepared in one of the furnaces mentioned in chapter vii, page 97. The phenolate passes down the "springing" or reaction tower, over the packing or plates, and the gas containing the CO_2, entering the bottom of the tower and travelling in an upward direction, comes into contact with the finely divided phenolate and decomposes it. No phenolate should be passed through the tower weaker than 15 per cent. of tar acids, and the rate of pumping to the top of the tower should be between 1½ and 2¼ gallons per minute. This speed will vary according to the type of tower used and the richness of the gas passing up that tower. It is advisable to use a gas containing not less than 19 per cent. of CO_2, by volume. Cases frequently occur, however, where it is not possible to obtain a gas containing more than 15 to 17 per cent. of CO_2, and in these cases it is necessary to reduce the speed of the pumping to somewhere in the neighbourhood of 1¾ gallons of phenolate per minute. It is very advisable to test the spent liquor as it runs from the separator, to find the percentage of tar acid it contains. The maximum amount allowable for a plant working perfectly is 0.5 per cent., and should this amount be exceeded, then it is time to look round the plant to see whether the gas is poor in CO_2 owing to the furnace wanting re-charging, or the charge burning hollow, or due to leaks in the gas main, or whether the speed of the phenolate is above that which it should be. It should be pointed out that care must be taken to prevent oil getting into the reaction tower with the phenolate, and time should be allowed for this to separate in the phenolate boilers. In order to keep the reaction tower in good working order, it should be steamed out at intervals of about eight weeks.

With reference to the manipulation of the CO_2 furnace, it is advisable to charge this piece of apparatus about every four hours, or even more frequently with some types of furnace, and in all cases to see that hollow places do not occur, and that the contents of the furnace are kept compact. This of course can be done by regular inspection, and, if a defect is found, using the poker intelligently. The coke should not be too large, about a size which will pass through a 1½-inch to 2-inch riddle or sieve. It must be of the best quality, as free as possible from water, sulphur, and clinker.

The tar acids and spent liquor leave the reaction tower at the bottom and are conducted to the two dividers (see chapter vii, page 94), and here the tar acids are separated from the spent liquor, the latter running to storage boilers, and the former to settling receivers. The tar acids are allowed to stand in these receivers for several hours, to settle out entangled spent liquor, and then run into the finishing tank in measured quantities, for treatment with a small amount of sulphuric acid. It is necessary to use this acid, owing to the fact that a complete decomposition of the phenolate does not take place in the reaction tower. The acid should be added carefully, with thorough agitation, until the mixture changes a blue litmus paper red. In this operation the acid not only decomposes the remaining phenolate, but assists in the removal of some of the water. It is advisable to use a B.O.V. of about 140° Tw. in this operation.

After the acid has been added, it is as well to carry out a laboratory test for the crystallising point, if crude carbolic is the quality under treatment, and in any case for the percentage of water. Should the latter be above 15 per cent. it will be necessary to add a little more acid to the contents of the finishing tank in order that it may be reduced. When the desired result is obtained, the acids are best removed to a storage tank by syphoning over into a blow-boiler and transmitting by compressed air.

With reference to the finishing of cresylic acid, it is necessary to remove as much water as possible before transferring to the storage tank or the still charge tank. The reason for this is that water is a difficult material to contend with during the process of distillation. If care be used, a large quantity of the entangled water may be removed by the use of acid in the finishing tank.

After the carbolic acid has been allowed to remain in the storage tank for a short time, it is ready for despatch, and is either barrelled direct from the tank or else pumped (or, better still, transmitted by compressed air) into railway tanks or tank boats. Of course it is necessary that a careful test be made in the chemical laboratory to determine the crystallising point and other constants of the acid before it is despatched, and it is also advisable to keep two large samples, say of a pint each, in case a dispute arises between the buyer and the seller. The specific gravity of crude carbolic acid varies between 1.050 and 1.065.

It is policy before submitting the cresylic acid to distillation to allow a further period of time for settling, to enable any entangled acid liquor to settle out, which, should it get into the still, would injure it, and also spoil the pitch. Furthermore, the distilled cresylic acid would not be improved by the sulphurous acid set free during the distillation. When the cresylic has settled sufficiently long, it is charged into the still, the fire lighted, or if producer gas is employed, this is turned on and ignited. The heat may be increased rapidly until such time as the dome of the still begins to get hot, when it is advisable to slacken the temperature of the furnace and work carefully until water and acid appear at the worm end. The rate of distillation must be carefully regulated, in order to avoid any risk of a boil-over. A mixture of water and acid comes over first, and this separates, after leaving the collecting box, in the separator described on page 106. If the cresylic acid has been carefully prepared, there will be very little oil in the first runnings. These first runnings consist to a large extent of poor carbolic acid, but in cases where the still is provided with a good fractionating column, it is possible to obtain a fair percentage of a moderately good carbolic acid. When a fractionating column is used, it is essential that no distillate be passed into the column until water discontinues. Immediately this takes place, then the by-pass is thrown out of gear and the vapours conducted into the fractionating column. The point at which the distillate is changed over from carbolic acid to cresylic acid must be determined for each particular batch of acid as it undergoes the course of distillation, and the chemist should receive samples occasionally. A usual method is to catch the carbolic fraction into barrels, and then change over to the cresylic receiving tank, cutting out the fractionating column at the same time by means of the by-pass. Some prefer to work each still charge to pitch, but this is a dangerous proceeding as a rule, the risk of burning the plates of the still being very great. It is far better to work several charges up to a determined point, running off the bottoms each time into a bottoms storage tank, and when sufficient has accumulated, to make up a still charge and submit to a re-distillation. If the bottoms are particularly rich in cresylic, it may be necessary to run off again into a bottoms tank, and so proceed until they become very viscid, when the final distillation is made with the object of working to pitch. The method of procedure must be determined by the chemist, or manager of the works, for his particular quality of cresylic acid. Care must be taken in working to pitch that the distillation is not carried too far. To over-run the point when pitch is formed will produce either pitch coke or an intermediate product which may be termed spongy pitch; the latter material is dangerous, as it is exceedingly liable to spontaneous combustion immediately the still manlid is removed, and it is also difficult to remove from the still. Pitch coke on the other hand is not liable to spontaneous combustion, but it has to be chipped out of the still, and during its formation the plates may become badly burned. Cresylic pitch is not of much value alone, and is generally mixed with the large quantities of coal tar pitch in the bays.

A 1500 gallon charge of well settled cresylic acid, if worked to bottoms and not pitch, will take about 24 hours to finish. The total yield of crude carbolic acid, possessing a crystallising point of about 46° Fahr., will approximate 9 per cent., that of ·98 per cent. quality cresylic 60 per cent., water 8 per cent., and bottoms 23 per cent. A mixture of bottoms, when distilled, will yield approximately 80 per cent. of cresylic acid, the balance being pitch and loss.

The cresylic acid as obtained from the still is not ready for sale. Distilled cresylic acid contains H_2S and other sulphur compounds, which give to it a very unpleasant odour, and it is necessary to remove these objectionable compounds before placing the acid upon the market. To remove these compounds the acid is air blown in the special tank described on page 107. The acid is transferred from the receiving tank, either by a pump or compressed air, to the air-blowing tank. Air is now passed into the acid by means of an air compressor, or else drawn through the acid by a steam ejector. The foul air must be dealt with according to the Alkali Act and therefore should be "burned" or passed through purifiers, and not allowed to escape into the atmosphere. As regards the length of time required to free the acid from sulphur compounds, nothing definite can be said, but as a guide to the learner, an average figure of three days may be taken. It is necessary for the chemist of the works to rig up a testing apparatus and submit samples occasionally to a very simple test, as described on page 251.

Crude cresylic acid is usually sold on the basis of 95 per cent. or 97 to 99 per cent. of tar acids, and it is necessary for the chemist to test each batch as finished for this content. The impurities will, of course, consist chiefly of (*a*) oil, (*b*) naphthalene, and (*c*) water. The specific gravity varies somewhat, generally being between 1.042 and 1.055.

With reference to a quality of cresylic acid termed "water white," this is not produced in the majority of tar distilleries, and will therefore not be dealt with in this book. The same remark applies to the manufacture of carbolic acid crystals.

DIRECTOR OF INDUSTRIES
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CHAPTER IX

PLANT FOR THE RECOVERY OF BENZOLS, NAPHTHAS, ETC.

Washing tanks—"blow-over" stills—"blow-over" still fractionating column—fractionating still and column—dephlegmator—condensing coil and tank—divider box—storage tanks.

THE plant necessary for the production of benzols and naphthas is complicated, and the designs used by distillers are numerous. It is not possible to describe them all in this book, and therefore a general description of suitable plant is given.

It is necessary before the light oils are worked up into what are termed "once run" products that they should be washed free from tar acids and pyridine. Washers for the recovery of tar acids are described on pages 88 and 108 and will not need a second description here. With reference to the removal of pyridine, this is carried out in tanks made entirely of cast-iron, cast-iron lined with lead, or wrought-iron; mild steel is frequently used in place of the latter. These tanks must be provided with an agitator, and the necessary gearing to manipulate it. The agitator may be of the archimedean-screw type or of the paddle type, and in the latter case horizontal paddles should be used in preference to vertical ones. The writer considers the archimedean-screw type of agitator the best kind to employ. A vertical washing tank must be covered in at the top, and should be made with a cone or dish-shaped bottom. An outlet for running off the pyridine acid and acid-tar should be placed at the apex of the cone, or the lowest portion of the dish bottom, and connected up to lead piping, which, in its turn, is connected to an acid-resisting metal valve (regulus metal). The position of the washer may be such that it is not necessary to use lead piping at all, but simply to connect the valve direct to the bottom. Paddle agitators of the horizontal type have the shaft running through stuffing boxes, and care must be taken that these are of a good make, otherwise there will be considerable trouble in connection with leaking.

Wood is the best material to use to cover in the top of a vertical washer, but cast-iron, wrought-iron, and mild steel are sometimes employed. Let in through the cover of the washer is a charge pipe, an acid supply pipe, a water-pipe, and also an inspection hole with a wooden cover. With reference to the water-pipe, the writer prefers to water-wash the contents through the inspection hole, using a piece of flexible hose. By this means the sides of the washing tank can be washed down with water before any agitation is carried out. The advantage of this will be discussed in the next chapter. A few inches above the bottom of the washer, an outlet pipe is attached, through which the washed oils are passed into storage tanks or to the stills.

Some tar distillers prefer horizontal washers, but in the writer's opinion these are not nearly so satisfactory as the type just described. It is not so easy to run off the acid tar and pyridine acid from a horizontal washer, or to wash the sides down thoroughly. Furthermore the draining of the pyridine acid and acid tar cannot be carried out so completely. It is absolutely essential to erect the washing tanks in an elevated position, and the best results are obtained if the height is such that the washed oils can be run by force of gravity into the storage tanks or still.

There are many works in which one washer is used for both the acid and the soda washes. This is not advisable, as there is a great risk of spoiling the oil during the soda wash. It is far better to erect two washers of the same size and constructed on the same plan, and use one for the acid and first water-washes, and the other for the soda and final water-washes. The acid tar is run to waste, and the pyridine acid into a receiving tank, which is also often used as a storage tank. As the acid tar is often almost solid, it is best to let it run into open ended tubs or other suitable receptacles for treatment before disposal. When a lot of pyridine acid has to be dealt with and it is desired to work it up for pyridine, it is advisable to put in storage tanks—lead-lined wooden tanks are most suitable. Fuller details of these tanks will be given in the chapter dealing with the plant for the working up of pyridine acid for pyridine.

Broadly, there are two kinds of still used in the process of recovering benzols and naphthas from tar oils. These are known in tarworks' terminology as "blow-over" stills and rectifying stills. The former type may be subdivided into fire-heated and steam-heated. In the case of light oil, and often with crude naphtha, the "blow-over" still is fire-heated, and in many cases it is not provided with a fractionating column, although it is a decided advantage to fit such a piece of apparatus to the still. Another type of "blow-over" still is steam-heated, and in most cases this kind is used immediately before working the oils through a rectifying still. Steam-heated "blow-over" stills and rectifying stills are always provided with fractionating columns.

Fire-heated "blow-over" stills are built similar in shape to a tar still and are constructed of ½-inch mild steel plates. The bottom is built concave, with a rise of approximately 2 feet 6 inches from the horizontal. To the bottom is riveted a channel plate, and this channel plate is also riveted to the shell of the still. It is advantageous to construct the bottom of the still of sketch plates or segments, and connect these to a circular crown plate on top. The dome of the still is built with a rise, the height of which will vary according to whether the dome is to carry the fractionating column or the fractionating column is to be supported upon joists. In the former case a rise of about 3 feet is necessary for a 9-foot diameter still, but in the latter a rise of about 12 inches for the same diameter is all that is requisite. The still should be provided with a tail pipe and run-off tap, a safety-valve, a trial or overflow tap, and an inlet stool, to which is connected the charge pipe. A manhole and lid must also be provided. If the fractionating column is not supported on the dome of the still, it is necessary to provide a cast-iron swan neck and connections, in order to conduct the vapours from the still to the fractionating column.

With reference to the fractionating column, this may be constructed either of cast-iron in the form of segments, or of mild steel, and is cylindrical in shape. Its diameter will vary a little, but average diameters may be taken as 2 feet 6 inches and 3 feet. In the case of cast-iron columns, each segment will have a perforated plate fitted into it, or cast on it and then drilled. Mild steel columns are fitted with a series of brackets from top to bottom, on which are supported the perforated plates (see Fig. 58). These plates should be roughly about 9 inches apart, and are perforated with ¼-inch holes at a pitch of 1 inch. There is also one hole having a diamteer of 4 inches cut in each plate. The plates are ¼-inch thick, and in the case of a mild steel column, its thickness may be ⅜-inch. If the still is exposed to the weather, a mild steel column is the best to use, as it is less liable to crack owing to atmospheric conditions, such as rain falling on the column during the time that it is working. Better results are obtained if the column is surrounded by a draught screen, built, say, of corrugated iron sheet; in fact this method should always be adopted in cases in which the still is erected in the open. At the top of the column a cast-iron vapour outlet is fitted, and this is connected in turn to the vapour pipe.

With reference to the setting of this type of still, the method given under the setting of tar stills on pages 36–44 will give the most suitable results.

Steam-heated blow-over stills (Fig. 58) are constructed of mild steel plate of a thickness varying between ⅜-inch and ½-inch; sometimes ⅜-inch plates are used for the shell and ½-inch for the ends in the case of horizontal stills. The best types of steam-heated blow-over stills are of the horizontal pattern. With reference to the size of this type of still this will vary considerably according to the amount of naphtha that is to be dealt with, but a good average is 9 feet in length and 7 feet 6 inches in diameter. The still is fitted with a casting, to which the run-off pipe is connected; also an inlet pipe stool; a 1-inch

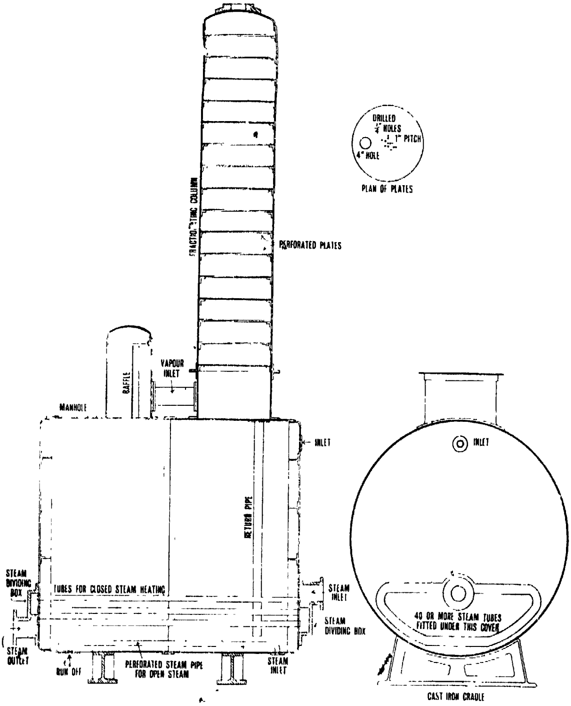

FIG. 58.—Diagram illustrating a Type of Steam-heated Blow-over Still with Fractionating Column.

to 1¾-inch open steam-pipe inlet, to which is connected a perforated steam-pipe; steam chests; a series of 1½-inch to 2-inch wrought-iron tubes for closed steam—these tubes being covered at each end by the steam chest covers; a manhole of the usual size, provided with a draw-up manlid; a safety-valve; and also a gauge of the glass tube or else of the refraction type, in order to indicate the level of the liquid in the still. Sometimes this kind of still supports the fractionating column; in this case a vapour dome, fitted with a baffle, is usually placed near the fractionating column and connected to it by a piece of cast-iron pipe. Fig. 58 illustrates one way of doing this. The fractionating column should be light and preferably made of wrought-iron or mild steel of about ⅜ inch thick; in fact the same type of fractionating column as that already described for fire-heated blow-over stills may be used. The number of plates contained within the fractionating column may be between 16 and 20.

If it is desired to do away with the vapour dome and baffle, a swan neck made of cast-iron may be used in its stead to carry the vapours into the fractionating column (see Fig. 59). The bottom of the column is connected to a wrought-iron return pipe of 2 inches in diameter, bent in the form of a U-seal, or, if straight, extending almost to the bottom of the still. If a cast-iron column is used, it is advisable to support it on stanchions and joists, but it may be connected either with a swan neck or vapour dome and baffle to the still, as desired. It is necessary to support this type of still on cradles. These may be of cast-iron or built of brick or concrete; the writer prefers cast-iron, as in his experience these have given the most satisfactory results.

Fractionating stills are generally of the horizontal type, constructed of ⅜-inch to ½-inch mild steel plates, and provided with fittings of a similar kind to those described for steam-heated blow-over stills. (See Fig. 59.)

With reference to the fractionating column, there are a number of types, and it is not possible to describe every one of them in this book. If it is desired to produce ordinary naphthas and benzols, a fractionating column containing about 20 plates, and having the last 6 segments water-cooled, will prove quite suitable, but, on the other hand, if it is required to produce benzol, toluol, and xylol, 95 per cent. distilling over within between ¾° and 1°, it is necessary to connect the fractionating column with a piece of apparatus known as a dephlegmator. This apparatus, together with condensers, is described later.

A great deal more care must be taken in choosing a fractionating column for a rectifying still. The ordinary perforated plate is not likely to give such good results as those plates which are fitted with special dispersing arrangements. What is desired in a fractionating column is to bring the hot vapours, which consist of a mixture of light and heavy compounds, in contact with liquid material, in order to remove from the vapours by a kind of washing the heavier substances from the lighter.

This can only be secured if each plate is arranged to carry a

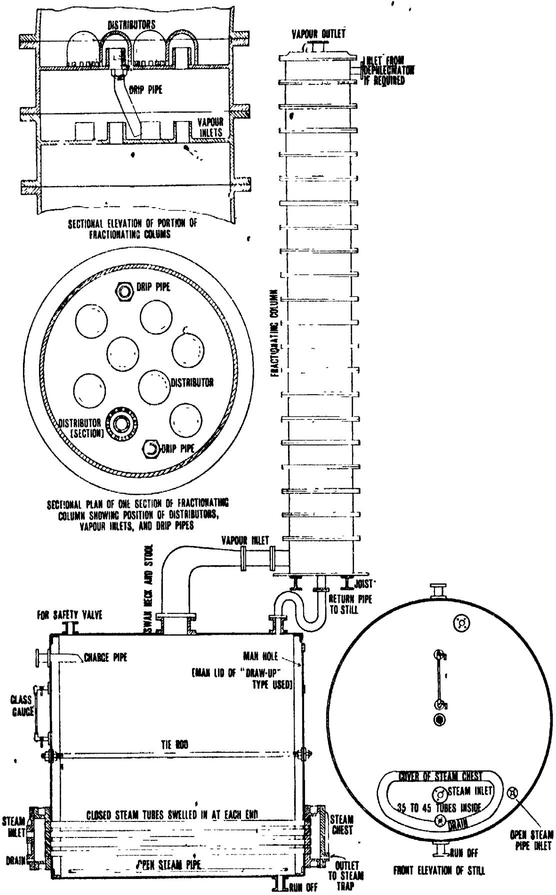

Fig. 59.—Fractionating Still and Column.

certain depth of liquid during the process of fractionation. With the ordinary perforated plate it is more difficult to secure this state of affairs than it is with plates provided with an arrangement which will keep a constant level of liquid, and allow the vapours, as they rise, to pass in a finely divided state through that liquid.

One of the best types of fractionating column which the writer knows of is shown diagrammatically in Fig. 59. This column, like most of the columns used for fractionating stills, is built up of cast-iron segments. The number of these segments will vary, of course, according to the degree of fractionation desired. If a dephlegmator is used, a column constructed of between 16 and 20 segments will prove quite suitable, but if it is desired to do without a dephlegmator, it is advisable to build the column of between 25 and 30 segments. The diameter of each segment may vary between 2 feet and 2 feet 6 inches, and the over-all depth between 8½ and 12 inches. The plate is cast on to the body of the segment, and the top of the plate is about 3 inches below the top of the segment. Each plate is provided with eight or more inlets, which conduct the vapours from the lower half of the segment. Over each of these inlets a cast-iron hood or disperser is placed; this disperser is beehive in shape, and has twelve openings ½ inch by ½ inch, as shown in Fig. 59. There are also provided two overflow outlets, to which are connected overflow pipes. The method of arrangement will be seen on referring to Fig. 59. The bottom segment of the column is provided with a vapour inlet of 4 inches in diameter, and this is connected by a swan neck to the still. There is also cast on this segment a 2-inch connection to which the return pipe is fitted. The return pipe is passed into the still, and should reach almost to the bottom, or else be bent in the form of a U-seal as shown in the figure. The top section of the column has a vapour outlet stool cast on to it, which may be 2 inches in diameter; to this is connected the vapour pipe which will lead either to the condenser coil or to the dephlegmator. If the column is not connected to a dephlegmator, it is very advisable to water-jacket the top six or eight sections. Should the column be connected to a dephlegmator, it is necessary to provide the top section with an inlet hole, to which is fitted the return pipe from the dephlegmator (see Fig. 59). This return pipe is made in the form of a U with one limb longer than the other, in order to provide a seal of liquid to prevent the vapours from entering the bottom portion of the dephlegmator.

Dephlegmators vary in construction, some being cylindrical, and others square or rectangular in shape. All of these types will give excellent results, but only the cylindrical shape will be described. It consists of a mild steel cylinder its diameter, as a rule, varying between 2 feet and 2 feet 6 inches and its length between 7 feet and 8 feet. Inside the cylinder, about 1 foot 6 inches from each end, are riveted two plates, into which are fitted a large number of copper tubes of similar diameter (between ¾ and 1 inch). Through these tubes a flow of water is maintained, and the vapours from the fractionating column pass round the tubes, the heavier vapours being cooled and returning to the fractionating column via the U-shape return pipe just described (see Fig. 60). The dephlegmator is

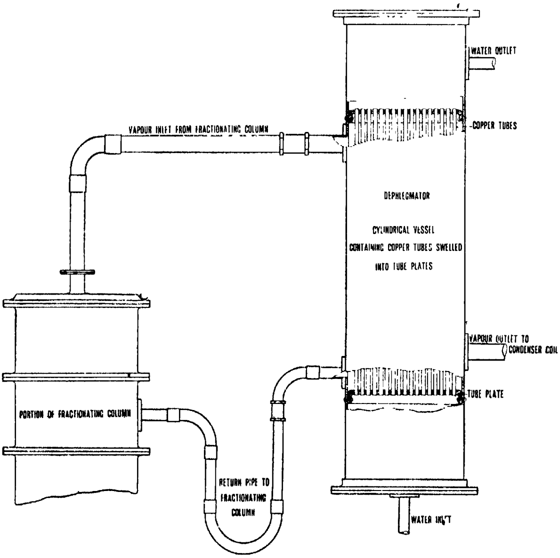
VAPOUR INLET FROM FRACTIONATING COLUMN
WATER OUTLET
COPPER TUBES
DEPHLEGMATOR
CYLINDRICAL VESSEL CONTAINING COPPER TUBES SWELLED INTO TUBE PLATES
VAPOUR OUTLET TO CONDENSER COIL
TUBE PLATE
PORTION OF FRACTIONATING COLUMN
RETURN PIPE TO FRACTIONATING COLUMN
WATER INLET

FIG. 60.—Diagram showing a Type of Dephlegmator and a Method of connecting to the Fractionating Column.

therefore provided with a vapour inlet at the top, which enters just underneath the top tube plate, and a vapour outlet near the bottom, just above the bottom tube plate. A return pipe is also fitted near the bottom, just above the tube plate. Water is introduced through the inlet fitted to the bottom of the dephlegmator and leaves by the outlet at the top.

After the vapours leave the dephlegmator, or, when this is not used, the fractionating column, they are conducted to a condenser. This condenser may be constructed of wrought-iron tubing, arranged in a number of laps placed in a cylindrical tank, or, especially in cases where a dephlegmator is used, of a cylindrical vessel inside of which are riveted top and bottom plates drilled with holes into which a number of tubes are fitted, very similar in fashion to the arrangements just described under dephlegmators. If it is desired to fit up a condenser coil of the usual type, it is advisable to have that coil made in one length of wrought-iron pipe. The diameter may vary a little, but one of 2-inch diameter will generally prove quite suitable. The total length of the tube will vary, of course, according to the condition of the water supply and the rate at which it is required to work the still. With a still working at an average speed of about 70 gallons per hour, 180 feet of 2-inch wrought-iron pipe will be quite sufficient. The over-all diameter of each coil may be 4 feet 6 inches to 5 feet, and the distance between each lap should not be less than 4 inches. At least 4 inches should be allowed between the outside of the coil and the inside of the condenser tank, and the top lap of the coil should be covered with about 6 inches of water when the coil is working.

The condenser tank is cylindrical in shape and fitted with water inlet and outlet pipes, drain cock, etc., as described on page 50 Connected to the condenser is a divider box of exactly the same pattern as that described on page 53 (Fig. 30). The outlet from the divider box, however, is connected up to several 1-inch pipes by means of T-pieces, in order to conduct the various fractions to their respective storage tanks.

Storage tanks may be square, rectangular, or cylindrical, according to convenience. In all cases they should be covered in and provided with a run-off tap, and also drain cock, through which any water which may settle out can be removed.

CHAPTER X

THE RECOVERY OF BENZOLS AND NAPHTHAS: FIRST DISTILLATIONS AND WASHINGS

Distillation of crude naphtha by steam or fire—distillation of light oil by fire—distillation of light oil fractions by steam or fire—distillation of light creosote by fire—washing crude benzol, crude solvent and crude heavy naphtha to remove tar acids and pyridine bases—a method of washing crude benzol—a method of washing crude solvent—a method of washing crude heavy solvent methods for the purification of crude benzol.

THE various qualities of benzols and naphthas are obtained from crude naphtha, light oil, and often from light creosote. It is necessary to wash these oils, or certain fractions obtained from them, free from tar acids and pyridine before the process of rectification can be carried out, and in the case of the heavier oils, and very frequently with crude naphtha, a first distillation by fire is carried out, as is described below.

Dealing with crude naphtha, this distillate contains chiefly benzene and its higher homologues, and on treatment and rectification yields principally 90's benzol and 50–90's benzol. Crude naphtha as pumped over from the receivers will contain approximately between 4 and 6 per cent. of tar acids and a varying quantity of pyridine bases. The tar acids are removed as described in chapter vii. Pyridine bases are not removed until just before the rectification process.

It is preferred by some to submit the crude naphtha to a distillation before washing out the tar acids. Others prefer to wash out the tar acids before distilling, and it depends on the circumstances existing in the works whether this is done or not. In any case, after the tar acids have been removed it is advisable to allow an hour or two for settling, in order that any entangled phenolate may settle out. The extracted naphtha is then submitted to a distillation. This may be conducted in a fire-heated still fitted with a fractionating column, or in a steam-heated still to which a similar apparatus is connected. Two fractions may be collected, the first being run into what is termed the crude benzol receiver, and the second into a receiver for crude solvent. The end of the first fraction is generally found by submitting a portion of the distillate as it runs from the worm end to a rapid distillation in a retort in the laboratory.

As soon as the test sample shows the first drop at about 110° C. the distillate is changed over into the crude solvent tank. The end of the second fraction is determined when the specific gravity of the distillate taken from the worm end indicates approximately .965 to .970 at 60° Fahr. On to the residue in the still, other material is often placed, or it is removed and kept for working up with heavier distillates at some other time. The methods of obtaining the change-over points just given are not always used, and it is sometimes necessary to vary these according to the requirements which may obtain in the works.

The steam-heated still in which this naphtha may be fractionated must be provided with an open steam coil, as it is necessary to assist the distillation with open steam after a certain point is reached. Generally, open steam is introduced into the still when the distillate at the worm end, on testing in the laboratory, commences to distil at about 95° C. If, however, high pressure steam is supplied to the closed steam tubes, the open steam may be introduced at a later period. Care should be taken when first passing the steam into the still not to open the valve too wide. If this is done it will generally cause the still to prime or, in other words, fill the fractionating column with the heavier material from the still. This, of course, is a serious matter, and will, if it occurs, generally spoil the operation. The valve should be opened very gently at first, say about one-quarter of a turn, and then the passage of steam gradually increased until the still works evenly. When open steam is introduced, it is necessary to pass the distillate, as it comes from the worm end, through a divider box, in order to separate the condensed steam from the oil. The closed steam is not discontinued during the passage of open steam, but it must be regulated according to the rate of distillation desired. With reference to washing the distillates for pyridine, this will be dealt with after considering the first distillations of light oil and light creosote.

In dealing with the light oil fraction, this should always be washed with caustic soda lye to remove any crystallisable crude phenol, and also the crude cresylic acid which it contains, before submitting it to a distillation by fire. Some distillers prefer to submit the oil to a fire distillation before washing for tar acids, but this method is, in the writer's opinion, a mistake, as some of the tar acids are lost in the bottoms. Details of the methods of washing are to be found in chapter viii, page 119.

It is absolutely essential, however, to distil the light oil by fire before passing it along to the rectification plant to obtain naphthas. This oil, when distilled in the fire still, which should in all cases be fitted with a fractionating column containing at least 15 plates, may be separated into two fractions and a residue, or one fraction and a residue. The quality of the oil will determine which of these methods is the best to adopt. If the light oil is divided into two fractions, then the change over point from the first to the second fraction is generally determined when approximately 25 per cent. has come over. With a large number of oils this point is also indicated when the distillate at the worm end shows a specific gravity of about .925 to .928 at 60° Fahr. This fraction may be termed "once run light oil A." The second fraction—"once run light oil B"—is complete when the distillate at the worm end shows a specific gravity between .990 and 1.000 at 60° Fahr. The residue remaining in the still is run to creosote, or to special storage tanks, to await the recovery of the naphthalene. Should it be necessary to remove from the light oil one fraction only, then that fraction is complete when the specific gravity of the oil at the worm end is about .980 to .990 at 60° Fahr. In this case also the residue is dealt with as just mentioned.

For the convenience of the still attendant, his "change over" points, and finishing points, are often given him to read at 100° Fahr. For example, if it is desired to finish the distillation at a specific gravity of 1.000 at 60° Fahr. then the still attendant should stop collecting when his distillate reaches .980 at 100° Fahr. Open steam is not used during the distillation of light oil by fire.

It is advisable not to work too many charges through the light oil still before submitting it to a cleaning process: ten times may be taken as a good average.

The distillate or distillates obtained from the light oil as just described are now washed free from tar acids, and then submitted to a further distillation, either in a fire-heated or steam-heated still provided with a fractionating column. In this operation the "once run light oil A" distillate may be separated into one fraction and residue, or two fractions and residue. If only one fraction has been distilled off the light oil, this may be separated into one, two, or three distillates and residue.

In the case of the "once run light oil A," if this is separated into one fraction, the whole of it is run into the crude solvent naphtha receiver, and the point at which the distillation is stopped is indicated when the specific gravity at the worm end reaches about .960 to .980 at 60° Fahr. When two fractions are made, the first one is mixed with the crude benzol and the second run to crude solvent. The change-over point from the first to the second fraction is determined in a similar manner to that given under the working of crude naphtha on page 138, and the end of the second fraction is found as mentioned above. Considering a case in which only one fraction has been distilled off the light oil, should it be desired to separate this into three fractions, then the end of the first fraction is determined as already described. The second fraction is stopped when the specific gravity reaches .940 at 60° Fahr. at the worm end, and the third fraction, which is termed crude heavy naphtha, is finished when the specific gravity of the distillate collected at the worm end reaches between .960 and .980 at 60° Fahr.

The " once run light oil B " distiliate, if separated into one fraction, is worked until a specific gravity of about .970 at 60° Fahr. is reached. This distillate is run into the crude solvent naphtha tank. If, however, it is desired to collect two fractions, then the end of the first is determined when the specific gravity at the worm end reaches about .930 at 60 °Fahr., and the end of the second when a test of the distillate collected as it runs from the coil shows .960 at 60° Fahr. The former is run to the crude solvent and the latter to the crude heavy naphtha receiver.

The residue in all cases is run to creosote, or else reserved for the recovery of naphthalene. If it is desired to carry out the distillation just described in a steam-heated still, open steam is introduced with care shortly after the distillate appears, and the supply continued until the end of the operation, closed steam of course being employed throughout the entire distillation.

The light creosotes from some tars are not rich enough in light oils to warrant a treatment for the recovery of these, but in some cases it is found that sufficient of the benzene homologues may exist in the creosote to warrant a distillation for the purpose of recovering a fraction from which these materials may be obtained. When this is the case the light creosote is submitted to a distillation in a fire-heated still provided with a fractionating column, and a fraction collected the amount of which will vary considerably, and the finishing point of which will have to be determined by the chemist on the works. After washing this fraction free from tar acids, it is necessary to submit it to a further distillation in a fire-heated still, separating into one or two fractions as is found advisable. The first fraction may be run to the crude solvent and the second to the crude heavy solvent receiver.

The crude benzol, crude solvent, and crude heavy naphtha must be submitted to a washing process to remove pyridine bases and impurities. The former substances are of value to the tar distiller, and in almost every case are recovered and refined. Before commencing a wash, it is advisable to examine the oil, whichever quality it may be, for tar acids, and if any exist they must be washed out. In all cases, before washing it is advisable to allow the oils to rest for a time to settle out entangled water. Pyridine is the first of a series of organic substances which correspond to the general formula $C_nH_{2n-5}N$, and it is represented by the chemical formula C_5H_5N. It possesses basic properties and combines easily with mineral acids, according to the following equations:—

$$\text{(a) } C_5H_5N + HCl = C_5H_5NHCl$$
$$\text{or (b) } 2C_5H_5N + H_2SO_4 = (C_5H_5N)_2H_2SO_4$$

A fuller description of the properties of pyridine and its chief homologues will be found in chapter xiii, pages 166-167.

Sulphuric acid is used in all cases to remove the pyridine bases, and the quality usually employed is ordinary B.O.V., of about 146° Tw. In one part of the operation it is used as supplied, and in another part it is diluted. After the pyridine bases are removed, a stronger acid known as D.O.V., of a specific gravity of approximately 167° Tw., is employed. It is then necessary to wash the oils with water, then with caustic soda lye, and finally again with water.

In all cases two washers should be employed, one in which to conduct the acid-washes and the other the caustic soda and the final water-washes. If the acid and soda washes are conducted in one washer, there is a great risk of some of the resinous matter produced by the action of the acid adhering to the sides of the washer suffering decomposition by the caustic soda and then being dissolved by the oil. Distillates from the rectifying still off oils to which this has happened will possess a peculiar unpleasant odour and will rapidly go off colour.

Dealing first with crude benzol, one method of washing this material is as follows: A quantity of B.O.V. at 146° Tw. amounting to between 1½ to 2 per cent. of the volume of the oil is slowly added to the charge of oil in the washer, while it is under vigorous agitation. The period of agitation may be between 20 minutes to half an hour. After this time has elapsed the contents of the washer are allowed to rest for about half an hour, and the greater part of the substance which settles out, known as pyridine acid, is run off into the pyridine-acid tank. After a further settling of about half an hour, any more pyridine acid which has separated should be run off, and then about ½ to 1 per cent. of D.O.V. slowly added to the oil, with agitation. The time occupied in agitating in this case may vary from 20 minutes to three-quarters of an hour, but care must be taken that the oil does not become too hot. After the agitation it is allowed to settle for about 10 minutes, and as much of the substance (known as acid-tar) as has separated removed. The resinification of hydrocarbons brought about by the action of D.O.V. is sometimes considerable, and the acid-tar formed often very rapidly solidifies to a "livery" mass, which will not flow, and which has a tendency to adhere to the bottom and sides of the washer. It is policy, therefore, not to lose any time, but to remove as much as possible before this state sets up. Further settlings of 10 minutes are given, and any more acid-tar which separates is run off. When the whole of the acid-tar has been removed—it should be noted that this material must not be run to the pyridine acid tank—the sides of the washer should be carefully washed down with a spray of cold or warm water. This will settle to the bottom, and is removed via the catch tank—in which is separated and retained any oil which may escape from the washer—to a neutralising tank, and from the tank to the drains. After this preliminary wash, the oil is washed with water until the washings are practically free from acid. It is a good plan not to agitate the oil with water when giving the first wash, but to spray water on to the surface of the oil and let it fall through it to the bottom of the washer. When the washing is completed, the oil is pumped, or run by force of gravity, into the second washer and treated with about ¼ to ¾ per cent. of caustic soda lye standing at 40° Tw. or thereabouts. The soda lye is allowed to separate out, and then run off, and after this the oil is washed with clean water until the wash waters react neutral to litmus. After a thorough settling, the washed oil may be run direct into the rectification still, or to a storage tank, to await treatment at a later date.

It is sometimes found advisable, in fact in the writer's opinion it is wise always, to wash the crude benzol with a little dilute B.O.V. before adding the D.O.V. This will ensure a complete removal of the pyridine bases. This dilute acid may be prepared by adding one part of B.O.V. to one part of water, and the amount added to the benzol may vary between ¾ and 1 per cent. The total loss of crude benzol by washing varies considerably according to the quality of the oil; however, a good average may be taken as 3 per cent. Some of the crude benzols contain unsaturated paraffin hydrocarbons, and these, of course, are acted upon by the sulphuric acid used in the washing, and will naturally increase the amount of loss.

In the preparation of pure benzols from a crude benzol, it is often necessary to remove a substance known as thiophene, and also some of its homologues. Thiophene is represented by the chemical formula C_4H_4S. It has a boiling-point of 84° C., a specific gravity of 1.07, is colourless, and possesses an odour similar to that of benzene. Concentrated sulphuric acid dissolves thiophene, and if the solution is treated with a trace of isatin, a dark blue colour is produced. As thiophene so closely approaches benzene with reference to its boiling-point, it is practically impossible to separate it by distillation. It is therefore necessary to remove it by chemical washing with concentrated sulphuric acid. In order to do this economically, it is wise to submit the crude benzol to a washing, as just described, and then carefully fractionate it and afterwards re-wash the fraction, which represents the once rectified benzol, several times with small quantities of D.O.V. It is essential of course to submit the once rectified benzol—after it has undergone several strong acid washes—to a test for thiophene in the chemical laboratory. When this test gives a satisfactory result, the material may be washed with water and caustic soda, and finally with water, as previously described.

With reference to the washing of crude solvent naphtha, the process is essentially the same as that already described for crude benzol. It is necessary, however, to use a rather larger quantity of acid, as there is generally a higher percentage of pyridine bases contained in this material, and in order to produce rectified naphthas of good colour. So that the finished products shall be perfectly free from pyridine and able to pass the Weber test for that substance, it is advisable to use some dilute acid, prior to adding the strong acid (D.O.V.) used in the final acid wash. The following is a good method of washing a crude solvent. For the first wash add about 1 per cent. of B.O.V. at 146° Tw. and agitate vigorously for between 20 minutes and half an hour. After the period of agitation, allow to settle to precipitate the pyridine acid, which is run off to the storage tank for further treatment. The second wash of about 1½ per cent. of B.O.V. is now given, the time of agitation being about the same. After the removal of the pyridine acid, the naphtha is submitted to a third wash with dilute B.O.V. This dilute B.O.V. may be prepared by taking one part of acid and one part of water, and the amount used should be about 1½ per cent. Thorough agitation is necessary, and the time should not be less than half an hour. This weak acid wash will completely remove all the pyridine. The contents of the washer should be allowed to settle, and the weak pyridine acid which precipitates run off to the pyridine acid storage tank. At this point it is advisable to submit a sample of the naphtha in the washer to the Weber test. (See chapter xix, page 248.) If it passes this test, a fourth wash with D.O.V. is given. The quantity of this acid, as a rule, need not exceed more than between ¾ and 1 per cent. It is sometimes necessary, however, to use rather more, but circumstances will have to decide this. The time occupied in agitating should not be prolonged: usually about 25 minutes is ample. After this the contents of the washer should be allowed to rest, to deposit acid-tar, and it is just as well to run this material off at intervals of about 10 minutes. If it is allowed to remain too long in the washer, there is a risk of its becoming so thick that it will not run through the outlet. The acid-tar should not be run to the pyridine acid storage tank, but to a separate receptacle.

At least 1½ hours should be allowed for settling before the water washing is commenced, and it is advisable to thoroughly wash down the sides of the washer, and also spray the water on the surface of the naphtha, allowing it to fall through it by force of gravity, before any water is agitated with the oil; the water which separates during this process is removed before agitation with clean water is commenced. Further water washes are now given with agitation, which must not be too vigorous. When the wash water comes away from the naphtha practically neutral, a short time for settling is allowed, and the drainings removed. The naphtha is then pumped, or allowed to run by force of gravity, into a second washer for treatment with caustic soda lye of about 35°–40° Tw. A large amount is not necessary, the quantity usually varying between ¼ to ½ per cent. After about 20 minutes' agitation, the contents of the washer should be allowed to settle thoroughly, the lye wash removed, and the naphtha then submitted to water-washes as already described. It is necessary that clean water be used and the last wash-water should come away from the naphtha quite neutral to litmus. When this is the case, the washed crude solvent may be removed to a storage tank or direct to the rectification still.

Many of the crude solvents when washed with strong acid deposit an excess of acid-tar, often of a very resinous nature. A good method of avoiding this is to submit the crude naphtha to a second distillation before washing with acid, *i.e.* distilling the crude solvent in a steam-heated still, and collecting practically the whole of it in one fraction. This fraction, when washed in a similar fashion to that just described, appears to give very little acid-tar in the final acid wash. There is also a great improvement as regards the odour of the rectified material. The total loss of crude solvent varies to a much greater extent than that of crude benzol; it may be between 5 and 13 per cent.

In washing crude heavy solvent, a good deal of discretion is necessary. This class of material will contain varying quantities of naphthalene, and in the washing, especially with D.O.V., some of this material becomes sulphonated and is lost; in fact, if not carefully conducted, the loss may amount to as much as 25 per cent. It is generally necessary to use some D.O.V. if a rectified heavy naphtha which will keep its colour when exposed to the light is desired. The method of washing is exactly the same as has already been described, and the average amount of B.O.V. used at 146° Tw. is 2¼ per cent.; of dilute B.O.V. (1 : 1) ½ per cent.; and of D.O.V. 1½ per cent. It is advisable to divide the quantity of B.O.V. so that three washes may be given with it, and with the D.O.V. two. A wash with caustic soda lye of about 35°–40° Tw. must not be forgotten, the amount used being between ½ and ¾ per cent., calculated on the volume of the crude heavy solvent. Water-washes must be thorough, and it is absolutely necessary to secure neutrality after the acid and soda washes.

According to English patent 10,066, 10th July, 1915, instead of giving crude benzol the usual preliminary washing with acid and soda it is distilled direct and the benzol vapour passed successively through sulphuric acid (160°–168° Tw.) and caustic soda solution (30°–40° Tw.). It is claimed that the process may be made continuous, that the washing is more effective, and that a substantial reduction in the amount of sulphur compounds is effected compared with other purification processes.

Crude benzol contains, among other impurities, a fair amount of carbon disulphide, and this objectionable substance is, in practice, removed in the process of rectification, as will be mentioned in the next chapter. J. A. Wilson, English patent 14,152, 6th October, 1915, claims that benzene can be freed from carbon disulphide, before or after rectification or treatment with sulphuric acid, by agitating with caustic soda (20°–25° Tw.) at a temperature below the boiling-point of the benzene.

An interesting process for the purification of benzol has been recently described.[1] The crude benzol is purified by first vaporising it by known means and then passing it through sulphuric acid and a caustic alkali solution successively, and then (after any further desired treatment) condensing the purified vapour by known or any convenient means. For this purpose an apparatus (see Fig. 61 for a diagrammatic illustration) is provided which consists of a still R, a dephlegmator S, and analyser T, all of known or convenient construction, a compartment for sulphuric acid D, a compartment for aqueous caustic alkali solution E, and a condenser U. By this method and means the purification process may, if desired, be made continuous, and the purification is carried out in a single process.

The compartments D and E are surrounded by a steam-jacket, by which this vessel is maintained at a temperature not less than that at which the benzol vapour enters, to avoid condensation of the vapour when within the vessel. The benzol first bubbles through the sulphuric acid, then goes down the passage B, and bubbles up through the alkali solution. Baffles are provided in the compartments D and E to arrest any liquid spray that may be carried by the benzol vapour.

The concentration of the acid solution is preferably 168° Tw. to commence with, and should be maintained as near as possible thereat if the best results are to be obtained, Good results can, however, still be obtained with a concentration of 160° Tw. Care should be taken that the caustic alkali solution is not or does not become of too high a concentration, as, owing to the rapid evaporation of the water, sulphite crystals are liable in that case to be formed and thus obstruct the clear working of the apparatus. A suitable concentration is 30° to 40° Tw.

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[1] English patent No. 10,066 of 1915. Gerald L. Moss and Simon-Carves By-Product Coke Oven Construction and Working Company, Limited, 20 Mount Street, Manchester. Date of application, 10th July 1915.

The pump V maintains a vacuum throughout the whole circuit, and the purified benzol is collected in Z.

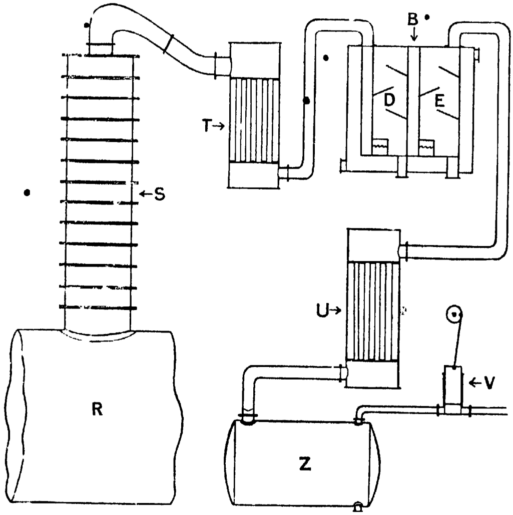

FIG. 61.—Moss and Simon-Carves' Apparatus for Benzol Purification.

Although the process is described as being carried out with the aid of an ordinary intermittent still, it will be understood that it may be applied equally to a continuous still, and in that case a complete unit may be provided for each fraction.

An ingenious method for removing sulphur from oils by the aid of a catalytic agent, and which is applicable to the purification of benzols and naphthas, has been invented by E. V. Evans of the South Metropolitan Gas Company.[1] The following is a brief description of it:—

The sulphur is eliminated as sulphuretted hydrogen by heating the oil in presence of hydrogen or gas containing free hydrogen and a catalytic agent or contact substance. In the case of an oil of suitable boiling-point, the vapour of the oil mixed with a small proportion of hydrogen (5 or 10 per cent. of its volume) may be passed over the heated catalytic or contact substance and the sulphuretted hydrogen removed from the vapour by absorption by any known agent, or the oil may be washed after condensation to the liquid form.

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[1] English patent No. 22,147 of 1914. Edward V. Evans and the South Metropolitan Gas Company, 709 Old Kent Road, London. Date of application, 6th November 1914.

The most efficient temperature of working is in the region of 400° to 500° C., for at this temperature the iron pipes which contain the catalyst or contact substance are not destroyed, and the velocity of the reaction is so high that a relatively small area of contact is required. Certain oils are, however, decomposed at these temperatures, and when this is to be avoided lower temperatures must be employed. To this end a relatively greater surface of contact will be necessary in order to bring about a similar effect as at 400° to 500° C. It is necessary, therefore, to determine with each particular oil the maximum temperature, below 500° C., at which the oil is not decomposed, and to allow sufficient contact with the catalytic or contact substance to ensure that practically the whole of the sulphur of the oil is converted into sulphuretted hydrogen.

The distillation of naphtha from crude coal tar is cited as an example of the application of the process. The vapours from the still are conducted to a furnace maintained at 450° C., in which steel or iron pipes are contained. A convenient arrangement for these pipes is in the form of a U. The vapours enter at the top of one limb and in descending are brought to the temperature of the reaction. To enhance this, the limb may be packed with non-combustible material. The catalytic material is placed in the second limb. Assuming that the rate of distillation is 50 gallons per hour, the volume of each limb of the U-tube should be about 7.5 cubic feet. A stream of hydrogen or coal gas is introduced at the inlet of the preheating tube or tubes and allowed to flow with the vapours at the rate of about 400 to 500 cubic feet per hour. Only a small portion of this hydrogen is actually used, and it is advisable to pump the hydrogen over in a closed circuit. The sulphuretted hydrogen produced as a result of the decomposition of carbon disulphide and sulphur compounds is washed from the condensed vapour by caustic soda solution, or it may be extracted direct from the vapour by means of an oxide of iron purifier kept sufficiently warm to prevent condensation.

In the case of an oil which cannot be distilled the catalytic substance may be introduced into the liquid oil, which is suitably heated while hydrogen is passed through it, or the heated oil may trickle over the catalytic substance while hydrogen is at the same time passing over it.

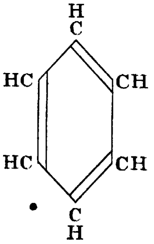
CHAPTER XI

THE RECTIFICATION OF BENZOLS AND NAPHTHAS

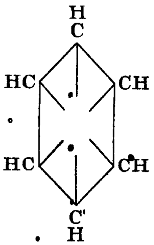
Chemical and physical properties of benzene, toluene, and the xylenes—fractionation of washed crude benzol—preparation of 90's and 50-90's benzol—fractionation of washed crude solvent—preparation of 90 per cent. at 160° C. solvent naphtha—preparation of heavy naphtha—preparation of 75° F. flash naphtha—preparation of 85° F. flash naphtha—preparation of commercial 90 per cent. at 120° C. toluol—preparation of commercially pure benzene, toluene, and xylene—works costs.

THE composition of crude benzol and also of crude solvent naphtha varies somewhat according to the quality and kind of tar from which they are recovered, but benzene, toluene, and the three xylenes occur in one or other of them in considerable quantity, and a brief description of the chemical and physical properties of these substances will not be out of place in this chapter.

Benzene (C_6H_6) is a colourless, highly refractive, mobile liquid possessing a peculiar but not unpleasant smell. Its specific gravity at 0° C. is 0.899; at 15° C., 0.882; at 20° C., 0.8791, and at 25 C., 0.876. When cooled in a freezing mixture it solidifies to a mass of colourless orthorhombic prisms which melt at 5.4° C. (corr.). Benzene boils at 80.36° C. (corr.). At ordinary temperatures 100 c.c. of water will dissolve approximately 0.01 c.c. of benzene. According to Kopp its specific



Kekulé.



Armstrong.

heat between 19° and 46° C. is 0.450. It is soluble in alcohol, ether, acetone, etc., and is an excellent solvent for resins, fats, ethereal oils, and many other organic compounds. Sulphur, iodine, and phosphorus are also soluble in benzene. With reference to the constitutional formula of benzene several have been suggested, but those of Kekulé and Armstrong have received the most support.

Benzene is a very stable substance, resisting the action of all the mild oxidising agents, and even when boiled with solutions of powerful oxidising agents, such as potassium permanganate or chromic acid, it is only very slowly acted upon. Dilute nitric acid has no action upon it, but strong nitric acid, especially in the presence of concentrated sulphuric acid, attacks it, forming nitro-compounds.

$$1.\ C_6H_6 + HNO_3 = C_6H_5.NO_2 + H_2O.$$
$$2.\ C_6H_6 + 2HNO_3 = C_6H_4.(NO_2)_2 + 2H_2O.$$

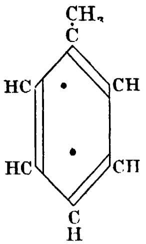
Concentrated sulphuric acid acts upon benzene very slowly at ordinary temperatures, but at its boiling-point it is acted upon more rapidly, forming benzene sulphonic acid—

$$C_6H_6 + H_2SO_4 = C_6H_5.SO_3H + H_2O.$$

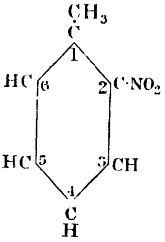
Fuming sulphuric acid converts benzene into benzene disulphonic acid, $C_6H_4.(SO_3H)_2$.

Chlorine and bromine act upon benzene in a very peculiar manner. In the presence of direct sunlight, or at fairly high temperatures, additive products are formed, such as hexachlorobenzene, $C_6H_6Cl_6$, and hexabromobenzene, $C_6H_6Br_6$; but in diffused light and at ordinary temperatures benzene is slowly attacked, substitution products being formed, such as chlorobenzene, C_6H_5Cl, dichlorobenzene, $C_6H_4Cl_2$, bromobenzene, C_6H_5Br, etc. Iodine appears to have very little action upon benzene.

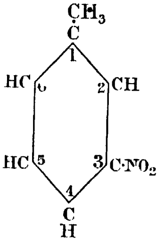
Toluene, methyl benzene, phenyl methane, $C_6H_5.CH_3$, is a colourless, highly refractive, mobile liquid, with an odour somewhat similar to that possessed by benzene. At 15° C. its specific gravity is 0.872, at 20° C. 0.866, and at 25° C. 0.8625. It solidifies below—100° C. forming colourless crystals which melt at —93.2° C. (corr.). The boiling-point of toluene is 111° C. (corr.). With regard to solvents and its solvent action it behaves very similar to benzene. It largely resembles benzene in its chemical properties, differing principally in those which are due to the presence of a side chain (the methyl group). The constitutional formula of toluene is written thus—



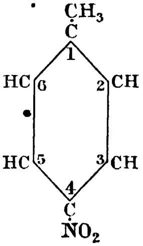
Its behaviour with sulphuric and nitric acids resembles that of benzene in so far as it yields sulphonic and nitro-derivatives. These compounds, however, exist in three isomeric forms, viz., ortho, meta, and para. For example, mono-nitrotoluol exists in three forms represented by the following constitutional formulæ:



Ortho.

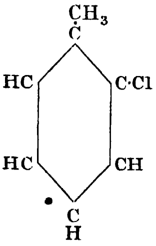


Meta.

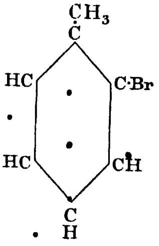


Para.

At ordinary temperatures and in diffused light chlorine and bromine act on toluene, producing substitution products by displacing the hydrogen of the benzene ring or nucleus, thus:

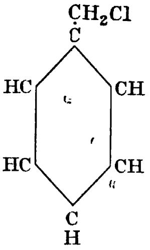


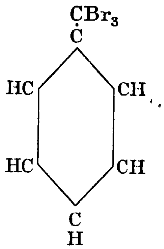
Ortho-chloro-toluene.



Ortho-bromo toluene.

If, however, toluene is acted upon by chlorine or bromine at its boiling-point, or in direct sunlight, substitution of hydrogen of the side chain or methyl group takes place, thus :

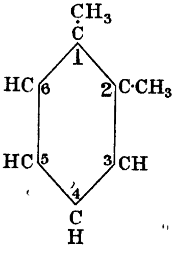

Benzyl chloride.

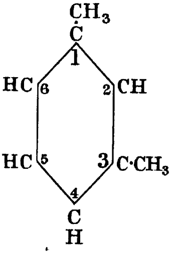

Benzo-tribromide.

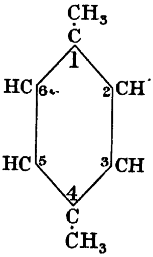
By the strong oxidising agents toluene is converted, with difficulty, into benzoic acid, the methyl-group or side chain being oxidised.

$$\underset{\text{Toluene.}}{2C_6H_5.CH_3} + 3O_2 = \underset{\text{Benzoic acid.}}{2C_6H_5.COOH} + 2H_2O.$$

Xylene, dimethyl benzene, $C_6H_4(CH_3)_2$, exists in three isomeric forms, viz., ortho, meta, and para. The constitutional formulæ of these isomers are :


Ortho-xylene.


Meta-xylene.


Para-xylene.

Some of its physical properties are given in Table XVIII ; and in Table XIX, constructed by Professor Richards and Mr C. L. Speyers, after making many careful observations, will be found some useful constants.

TABLE XVIII

Isomer.	Specific gravity		Melting-point, corr.	Boiling-point, corr.	Solubility in		
	At 0° C.	At 25° C.			Water.	Alcohol.	Ether.
Ortho	0.8932	0.876	– 29° C.	142° C.	Insol.	Sol.	Sol.
Meta.	0.8810	0.863	– 54° C.	138.5–139.5° C.	Insol.	Sol.	Sol
Para.	0.8801	0.859	15° C.	137–137.5° C.	Insol.	Sol.	Sol.

TABLE XIX

Substance tested.	Boiling-point in Deg. C.	Density at 20° C., compared with water at 4° C.	Surface tension at 20° C., in milligrammes per millimetre.	Compressibility at 20° C. × 10^6.
Orthoxylene .	144.0	0.8811	3.09	60.0
Metaxylene .	139.0	0.8658	2.96	63.5
Paraxylene .	136.2	0.8611	2.92	65.2

The three isomeric xylenes are colourless liquids possessing aromatic odours dissimilar to those of benzene and toluene. Their behaviour with concentrated sulphuric and concentrated nitric acids is very similar to that of toluene, sulphonic acids and nitro-compounds being formed. In the case of the para isomer it is necessary to use fuming sulphuric acid to obtain the sulphonic acid. Oxidising agents act upon the three isomers with moderate ease forming the toluic and phthalic acids by oxidising, in the former case one and in the latter case both of the methyl groups. Chlorine and bromine act upon the xylenes in a similar manner to the way in which they act upon toluene.

The chief products obtained by the rectification of crude benzol are 90's benzol and 50–90's benzol, and by a second rectification commercially pure benzol, which will yield about 95 per cent. within ½ to ¾ of a degree. Crude solvent naphtha on rectification will yield a large number of products, many of which are specially made to the specification of buyers. There are several grades of solvent naphtha, the chief of which is known as 90 per cent. at 160° C. Some of the other grades obtained are solvent naphtha yielding 95 per cent. at 165° C. or 90 per cent. at 190° C., and also those possessing flash-points of 75° and 85° Fahr. (Abel's close test). Commercial toluol is also obtained from crude solvent naphtha, and, by a second rectification, commercially pure toluol and commercially pure xylol. Crude heavy naphtha will yield various grades of heavy naphtha, the quality, specific gravity, flash-point, and distillation of which will vary according to the requirements of the buyer.

It is not possible to give here full particulars as to how all the products that may be obtained from these materials are prepared, but brief consideration will be given to the method of producing some of the chief products.

Dealing with crude benzol with the object of making 90's benzol, a charge of washed crude benzol is run into the rectifying still and closed steam turned on. When the contents of the still become heated throughout, the steam is slackened a little and the worm end carefully watched. As soon as liquid appears at the worm end, the steam should be regulated to a degree which will allow of the distillate running continuously, and not too fast. The material which comes over first from the washed crude benzol is termed "fronts," and contains a considerable quantity of carbon disulphide (CS_2). This must not under any circumstances be mixed with the 90's benzol fraction which follows the "fronts," but allowed to run into a separate receiver for further treatment. When the distillate at the worm end reaches a specific gravity of .890 to .898 at 60° Fahr. the tap on the "fore-runnings" or "fronts" main is closed, and that on the 90's benzol main opened, in order that the condensate may run into the 90's benzol tank. Distillation is now proceeded with until a sample collected from the worm end, and submitted to a test in the chemical laboratory, does not begin to distil until 100° C. is reached. It is of course necessary to make tests in the laboratory from time to time in order to guide the stillman. When the point just mentioned is reached, the flow of the distillate is cut off from the benzol tank and allowed to run into another receiver. When the distillate collected at the worm end is tested in the laboratory, and does not commence to boil until 130° C. is reached, the distillation is generally stopped, and the residue either run to a storage tank to await treatment with further bottoms, or on to it is charged some washed crude solvent.

If it is desired to produce 50's–90's benzol, then the 90's benzol fraction is cut a little earlier (about the point when a sample from the worm end on testing shows no distillate until a temperature of 95° C. is reached) and a fraction collected from this point until one is reached at which the distillate, when tested in the laboratory, does not commence to boil until about 120° C. is reached. This fraction is run to a special 50's–90's tank, to be dealt with later. Sometimes this quality of benzol is made by adding to the fraction collected some lighter material. At times, however, the fraction itself will yield benzol answering to the tests required, *i.e.* 50 per cent. at 100° C. and 90 per cent. at 120° C. The residue in the still is removed to a storage tank to await treatment with other bottoms, or else washed crude solvent is charged on to it.

With reference to the methods of making 90 per cent. toluol and also commercially pure benzene, toluene, and xylene, a brief description is given a little further on.

The washed crude solvent is charged into an empty rectification still or else on to the residue from a distillation of crude benzol. Distillation is commenced by the use of closed steam, and the first fraction is collected until a sample taken from the worm end and tested in the laboratory begins to boil at about 100° C. This fraction is generally run into the crude benzol storage tank for working up with another batch. For some classes of benzol, however, this fraction may be run into the 90's benzol receiver. It is necessary to introduce open steam shortly after the distillation commences, but it is not advisable to do this until absolutely essential, and when it is, the steam must not be turned on too rapidly. If it is desired to make 90 per cent. at 160° C. solvent naphtha, the end of the next fraction is determined when a sample tested at the worm end shows a specific gravity of about .895 at 60° Fahr., or, if submitted to a distillation test in the laboratory, does not begin to boil until 160° C. is reached. It is advisable when working for this, and even other qualities of naphtha, to occasionally test the material in the receiver after a thorough stirring up. For instance, in the case of solvent naphtha, to find what percentage is given off at 160° C., in fact, some stillmen prefer to have their tank tested, as the collection of this fraction comes to a close, for the precentage of distillate yielded at 160° C., rather than making tests at the worm end. It is necessary of course to discontinue running the distillate into the solvent naphtha tank as soon as the contents of that tank yield 90 per cent. at 160° C. when tested in a retort.

After the solvent naphtha fraction has finished coming over, the distillate is turned into another receiver. This fraction yields what is known as heavy naphtha, and the quality of this naphtha will vary according to how far the distillation is carried, or whether one or more fractions are collected. If it is desired to make a very heavy naphtha, giving about 60 per cent. at 190° C., then the distillation is finished when a sample at the worm end shows a specific gravity of .980 to .990 at 60° Fahr. Other qualities of heavy naphthas may be prepared by stopping the collection of the distillate at an earlier point. The residue left in the still is either run to creosote or else to a special tank, to be worked for naphthalene.

If it is desired to manufacture from the crude solvent fraction a naphtha possessing a flash-point of 75° Fahr. (Abel's closed test), and giving 90 per cent. at 160° C., then the following method is adopted. The distillation is commenced and the lighter portion is turned into the crude benzol tank, as already described, and then a further fraction is collected until a test of the material taken from the worm end shows no distillate until 130° to 133° C. is reached. This fraction is run into a special tank for re-distillation, or into the solvent naphtha tank, according to conditions obtaining in the works. The distillation is continued from this point until a sample collected from the worm end does not begin to distil until about 152° C. is reached. This fraction will give a 75° flash naphtha with a distillation test as already mentioned. The remaining material in the still may be worked for heavy naphthas.

Should it be required to manufacture a solvent naphtha yielding 90 per cent. at 165° C. and possessing a flash-point of 85° Fahr., then the crude solvent is worked first of all for the lighter fraction, as mentioned above, and then a second fraction is taken off, the end of which is determined when the distillate at the worm end, on testing in the laboratory, does not begin to distil until between 140° and 142° C. Between this point and that at which the distillate at the worm end when tested yields 45 per cent. at 165° C. the desired fraction is obtained. The residue in the still is worked for heavy naphthas as previously described.

In making these two qualities of solvent naphtha, a great deal will depend upon the rate of distillation, construction of fractionating column, etc. The slower the rate of distillation the larger the quantity of special material obtained from the charge. It is a very good plan to collect the fraction in, say, 50 or 80-gallon drums, as this will avoid the risk of spoiling the whole. A sample may be taken from each drum, bulked and tested, and then, if necessary, the contents of certain drums may be cut out before bulking.

Commercial toluol yielding 90 per cent. at 120° C. is obtained as a rule from crude benzol. This fraction is collected between the point at which a sample of the distillate, when tested, yields nothing until 100° C. is reached, and a further sample when tested does not commence to distil until 120° C. is attained. This point will vary a little according to the quality of the crude benzol.

In the manufacture of commercially pure benzene, toluene, and xylene, the method of procedure has to be varied somewhat, it being necessary first of all to distil the crude benzol into two or three fractions, and then to re-distil these fractions. In the first distillation the crude benzol is separated into a " fronts " fraction in the manner already described, and then a first fraction is collected until a test of the distillate leaving at the worm end yields nothing until 95° C. is reached. The second fraction is collected between this point and that at which a sample of the distillate collected from the worm end and tested does not begin to distil until 120° C. is reached. A third fraction may be collected, or the residue run to a tank for distillation with other bottoms. The first fraction is submitted to a further distillation in a still provided with a dephlegmator. It should be added here that if desired the crude benzol need not be washed before the first distillation, but the washing be carried out on this fraction and the second fraction obtained in the manner already mentioned. In washing like this, less resinous material is obtained and generally a better quality of product is secured. During the distillation of the first fraction for commercically pure benzene, it is necessary to keep the water in the dephlegmator at a temperature of about 60° Fahr. It is often essential to separate a little forerunnings, " changing over " when a sample collected at the worm end and tested does not commence to boil until 80° C. is reached. The process is continued and the distillate, and also the contents of the receiver, are tested throughout the operation in order to keep the fraction as close as possible to the desired distilling range, viz., one which will yield 95 per cent. within about three-quarters of a degree. The finishing point is generally determined when a sample of the distillate collected as it leaves the worm end and tested does not yield a drop until 81.5° C. is reached. Another quality of commercially pure benzene which drops at 79.5° C. and distils all over under 1° is prepared by collecting a fraction between the points at which a sample collected at the worm end and tested drops at 79° C. and another sample which when tested drops at about 80.5° C. Some manufacturers prefer to collect the distillate in 50 or 80-gallon drums and then test the drums and make a suitable mixing. This is a very satisfactory method. Commercially pure benzene should commence to boil at 80.5° C. and yield 95 per cent. at about 81.3° C.

The second fraction obtained from the crude benzol is worked up together with any residue from the first fraction for commercially pure toluene. Water is allowed to run through the dephlegmator until a sample collected at the worm end and submitted to a distillation shows nothing until about 109° C. is reached. At this point the distillate is " changed over " and the fraction just obtained may be worked up with other material for commercially pure benzene. The water supply is now shut off from the dephlegmator, and that contained in the apparatus allowed to get hot. Care should be taken of course to control the steam supply to the still, in order that the distillate does not flow too quickly. The distillation is continued until a sample collected at the worm end and tested does not begin to boil until a temperature of 110.5° C. is reached. Another method of working for the commercially pure toluene fraction is to commence collecting when a sample taken from the worm end and tested commences to distil at 109° C. (or 110° C. or 111° C.), and then work the still very carefully until the distillate as it leaves the worm end ceases to yield 95 per cent. within 0.8 of a degree from the chosen collecting point. The distillate may be collected into one tank and frequently tested, or, better, in drums which are dealt with as described under commercially pure benzol. Commercially pure toluene may also be manufactured from 90 per cent. toluol by a similar method to that just described. It should commence to boil at 111° C. and yield 95 per cent. at about 111.8° C. Some buyers demand a grade which drops at 109° C. and yields 95 per cent. at 110° C., others one which drops at 109.8° C. and yields 95 per cent. at 110.8° C.

Commercially pure xylene is obtained from the residue left from the distillation of pure benzene and pure toluene. These bottoms are worked up in a still provided with a dephlegmator, but almost all the water in the dephlegmator is removed so that the remainder will be converted into steam. The fraction collected for pure xylene comes over between the point at which a sample collected at the worm end and tested in the laboratory does not distil until a temperature of about 136.5° C. is reached, and that at which a further sample when tested shows no distillate below about 139° C. These points will vary a little according to the grade required. This product is a mixture of ortho-, meta-, and para-xylenes, and varies a little in test. A frequent requirement is, boiling-point 136.5° C., 95 per cent. off at 139.5° C., and another, boiling-point 136° C., 90 per cent. off at 139.5° C. and 95 per cent. off at 140.5° C.

In making these pure products, great care is necessary as regards the speed at which the still is worked. The steam supply must be so regulated that priming does not take place. The water which is passing through the dephlegmator must be kept at a constant temperature. It is necessary that the material should be thoroughly washed with acid, etc., before placing in the still. The best results are obtained if the still is provided with high pressure closed steam, so as to reduce the employment of open steam to a minimum.

For the guidance of the student the following average figures showing the cost of labour, chemicals, and steam to produce 1 gallon of rectified material are given. It must be clearly understood that figures like these will vary in different works according to local conditions, state of the chemical market, etc. To produce 1 gallon of 90's benzol, 0.48d.; 1 gallon of 90 per cent. at 160° solvent naphtha, 0.56d.; and 1 gallon of heavy naphtha, 0.59d.

CHAPTER XII

PLANT FOR THE WORKING UP OF PYRIDINE FROM PYRIDINE ACID

Pyridine acid tanks—egg—neutralised pyridine acid still—condensing coil and tank—pyridine water receiver and drying tank—caustic soda tanks—lime slurry tank—pyridine rectifying still—fractionating column—condensing coil and tank—still "bottoms" tank.

THE plant required for the working up of pyridine acid for pyridine will be dealt with under two heads, viz.: (*a*) That required for the manufacture of crude pyridine, and (*b*) that for the manufacture of rectified pyridine. Dealing with the plant for the manufacture of crude pyridine, there are several methods in vogue. One of these is to manufacture the crude pyridine during the process of making ammonium sulphate. This process requires a plant similar to that used for the manufacture of the latter material, as far as the still, liming apparatus, saturator, or cracker box, etc., is concerned. The cracker box is charged with diluted and clarified pyridine acid of a strength of about 50° Tw. instead of diluted B.O.V. A connection is fitted to the cracker box to conduct away the aqueous pyridine vapours that distil off owing to the heat of chemical reaction between the ammonia and the sulphuric acid, which is in loose combination with the pyridine bases. These vapours are conducted to a suitable condensing coil, and from there to a pyridine water-tank, and the poisonous non-condensible gases are conducted away for treatment by one of the approved methods. The weak pyridine water is allowed to rest, any oil which separates is skimmed off, and the pyridine water is then distilled until about one-third of its volume has been collected. From this point the plant and process resembles that described in this and the following chapter.

For the working up of pyridine acid by a more general process than that just described, the following pieces of apparatus are required: Lead-lined wooden tanks for the dilution of the pyridine acid; a large egg; a still constructed of wrought-iron or mild steel and provided with suitable fittings; a condenser coil and tank; a pyridine water receiving tank; a pyridine springing and drying tank; one or more caustic soda tanks; a lime mud tank; and suitable staging, tackle, etc.

The lead-lined tanks, or tanks for dealing with the pyridine acid, may be of any suitable shape, and constructed of wood or mild steel lined with, say, 5 lb. or 7 lb. chemical lead. If convenience will allow, they should be fairly deep, in order to render easier the skimming off of the resinous matter which comes to the top during the process. They may be erected on the ground level, and provided with a connection near the bottom for running off the clear pyridine acid into the egg.

The egg may be constructed of wrought-iron or mild steel, and, if desired, lead-lined. In the writer's experience a mild steel egg has proved quite suitable, and very little corrosion seems to take place, provided it is well drained and steamed out after each operation. The size of the egg will vary a little, according to the bulk of material which has to pass through it; but a good average capacity is 400 gallons. It should be provided with a pressure gauge; safety-valve; a 1-inch air inlet; a 1-inch steam inlet; a 2-inch outlet-pipe, which dips into a small dish made in the lower part of the egg and almost touches the bottom; a 2 inch pyridine acid inlet; and at the bottom on one end a 1-inch drain-pipe and valve.

In order that the diluted pyridine acid may run into the egg by force of gravity, this piece of apparatus should be erected just below ground level. It is advisable to dig a sump deep enough to allow for a three-gallon bucket to be placed below the drain-pipe. The hole into which the egg is placed, and also the sump, should be brick-lined, and just sufficient space allowed in order that the sides of the apparatus may be inspected: about 4 inches clearance is sufficient. It is advisable to keep this piece of apparatus just off the bottom, supporting it at intervals on non-absorbent bricks which have been treated with an iron protective compound. It is a good plan to coat the whole of the outside of the egg with a bituminous iron protective paint, to prevent rusting.

For the distillation of dilute and neutralised pyridine acid, a still (Fig. 62) constructed of wrought-iron or mild steel plates, about ½-inch thick, is quite suitable. The bottom of the still should be dished or, better, of the shape of an inverted cone. At the bottom of the dish or the apex of the cone a 12-inch treacle valve or gate valve should be fitted. It will be found that a still with a cone-shaped bottom will discharge the lime mud easier than any other shape. The dome of the still is constructed with a slight rise. On the centre of the dome is fitted a cast-iron swan-neck stool and swan neck. If desired, however, a 3-inch wrought-iron pipe may be used instead of the swan neck and swan-neck stool for the purpose of conducting the vapours to the condensing coil. A manhole 18 inches by 12 inches and a draw-up lid should be arranged for on the dome of the still. The charge-pipe will enter the dome of the still and should project a little on the inside; close to the point of entry should be fitted a cast-iron gland cock. A steam-pipe also enters the dome and runs almost to the bottom, where it is connected to an open steam coil. This coil will have to be arranged according to the shape of the bottom; it is advisable to place it as near the bottom as possible, and also, if it can be managed, to arrange for two laps. The diameter of this coil and the steam-pipe supplying it will vary according to the size of the still. As a precaution, a small safety-valve of suitable type may be fitted to the still dome, or to the swan neck. In order to wash away any lime slurry which may lodge on the bottom, particularly near the steam coil, it is as well to provide a 1-inch or 1½-inch water supply, to which may be connected a piece of flexible hose. After the still has been discharged and is cool, water may be played by means of the hose through the manhole, and by this means the still can be thoroughly washed out after each operation.

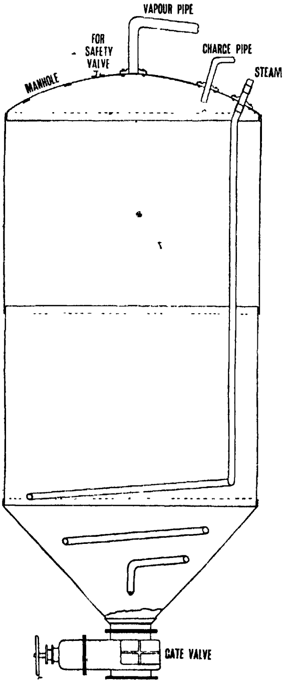


Fig. 62. - Still for the Distillation of Neutralised Pyridine Acid.

Connected to the vapour pipe of the still is a condenser coil, composed of a number of laps of wrought-iron pipe, circular in plan. This coil will vary in diameter according to the size of the still to which it is fitted. For instance, a still of a total capacity of about 1500 gallons would require a condensing coil of 3 inches in diameter and about 150 feet long. The distance between each lap should not be less than 4 inches, in order to allow a free circulation of water, and the distance between the edge of the condenser coil tank and the outside edge of the coil should be about 6 inches. A cylindrical wrought-iron tank constructed of ¼-inch plates is used to contain the coil. This tank is provided at the top with a water outlet and a water supply pipe, which should reach to within about 2 inches of the bottom. The end of the condenser coil may be put either through the bottom or the side of the tank, and is connected up to a delivery direct into the pyridine water receiver. It is as well to place at the bottom of the condenser tank a 1-inch drain tap, in order that the water may be removed if the tank or the coil require repairing.

For the collection of the pyridine water which runs from the condenser coil, a square, cylindrical, or rectangular tank may be used, according to convenience. This tank may be constructed of wrought-iron or mild steel plates, and should be covered in at the top with a wooden cover, which can be easily removed. It should be provided with a 2-inch run-off tap. In many cases it is convenient to use this receiver for the purpose of separating the pyridine from the water and afterwards drying it. If it is not convenient to do this, then a further tank will be required. This tank will of course have to be connected to the receiver and provided with two 2-inch run-off taps, one for the removal of spent soda and the other for dried pyridine, and also an inlet pipe to convey caustic soda to the contents of the tank during the drying operation. It may be constructed of mild steel plates, or of wood, lead-lined.

In the process of drying pyridine, strong caustic soda lye is required, and it is necessary to provide a tank for holding this. A further tank will be required, into which the dilute caustic soda lye may be run after the operation. If solid caustic soda is used to prepare the strong solution, then the strong lye tank must be provided with a grid, the bottom of which must be just covered with water when the tank is, say, three parts full. This grid is required to support the split drum of solid caustic soda. The process of dissolving will go on mechanically, especially if a small open steam coil is placed in the tank and the water warmed. Some manufacturers prefer to use liquid caustic soda of 90° Tw. If this material be employed, then it is not necessary to place a grid in the strong lye tank, as this quality of soda may be run out of the drums into the tank. In order to transport the strong caustic soda lye into the pyridine drying tank, an egg or blow boiler is required (some prefer to use a pump, but this plan cannot be recommended). If convenient, the weak pyridine acid egg may be employed for this purpose. If this method is not convenient, then a rather smaller egg may be put in.

A tank is required into which the lime slurry from the pyridine still may be run after the completion of an operation. This tank should be placed immediately underneath the still, and should of course be of sufficient size to contain easily the whole discharge. As this slurry is generally very wet, and a certain amount of water is dropped on to it during the washing down of the still, it is a good plan to build into the tank a filter bed, similar to that described in the manufacture of caustic soda (chapter vii, page 104). This will materially assist in the separating of the water from the slurry. The slurry is dealt with in a very similar fashion to the lime-mud from the causticisers, and should it be necessary, owing to circumstances, to produce a very stiff mud before removing from the works, then a centrifugal machine may be required to deal finally with the material.

With reference to the position of the various pieces of plant described, it is necessary that the still be erected of sufficient height to allow the condenser coil and tank, and also the pyridine water and drying tanks, being placed above ground level. The pyridine drying tank should be of such a height from the floor that drums, carboys, or barrels may be filled from it by force of gravity through the run-off tap. The lime slurry tank may be placed on the ground level, or a little above it, according to convenience. The caustic soda tanks should be on the ground level, and the egg, if one is put in for dealing with the caustic soda lye, should be placed in close proximity to the tanks and just below ground level. Over the caustic soda tanks and the pyridine drying tank a runway should be placed, on to which a chain block and pulley is fitted for the purpose of hauling up caustic soda drums, etc. Necessary staging, made of wood, may be erected round the tanks for the convenience of the workmen attending the process. Fig. 63 shows diagrammatically one method of arranging the plant.

For the rectification of crude dried pyridine, the following are the chief pieces of plant required: A wrought-iron or mild steel still with fittings; fractionating tower; condenser coil and condenser tank; receiver or receivers (some prefer working into small drums or carboys), and one or more bottoms tanks.

The still may be constructed of ½-inch plates. The bottom should be concave and connected to a channel plate in a similar manner to that described under tar stills. A suitable run-off or tail pipe is fitted to the still for the discharge of bottoms. The dome of the still should have a slight rise, and in the centre of the same a swan-neck stool and swan neck should be fitted. A charge-pipe is connected to the still at the top, and it is also provided with a manhole and draw-up manlid. It is advisable to fit a safety-valve to the still. The still settings, flues, fireplace, etc., are built in a similar fashion to that described under tar stills; but it must be borne in mind that the top of the flue should be just below the level of the liquid left in the still at the finish of the operation, otherwise there is a risk of the still plates getting burnt.

Connected with the swan neck is a small fractionating tower or column. This tower may be cylindrical in shape and built of wrought-iron. Inside the column a series of perforated plates are fitted. The number of these plates need not be large, say between 10 and 15. One constructed on a similar plan to that shown in Fig. 58 will prove quite suitable. The column is provided at the bottom with a U return pipe, which is led into the still, and at the top with a vapour pipe which is connected to the condenser coil.

With reference to the condenser coil, this is best constructed of lead. It should be properly stayed inside the condenser tank, which is constructed of wrought-iron. The usual water supply and outlet arrangements and drain tap are fitted to the tank. The end of the coil is connected to a small observation tank, which may be constructed of wood and lead-lined, and provided with an outlet, which may lead to receivers, or through which the distillate can be run into carboys or drums.

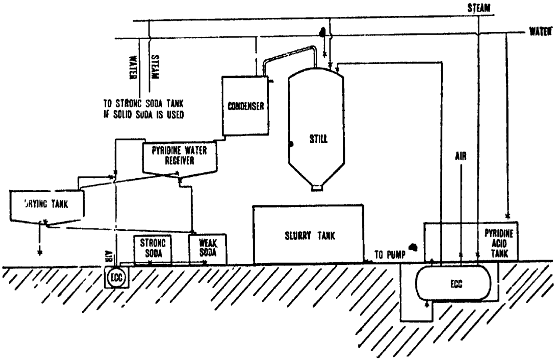


FIG. 63.—Diagrammatic Illustration of One Method of arranging a Recovery Plant for Crude Pyridine.

Tanks for the storage of still bottoms may be constructed of wrought-iron or mild steel plates, and built of any suitable shape. They should of course be covered, and provided with a manhole and lid, charge-pipe, discharge-pipe, and air outlet. The latter is necessary to let out the air when running in the bottoms. These tanks may be placed in any suitable position near the still, according to convenience.

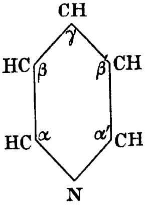
CHAPTER XIII

THE RECOVERY AND RECTIFICATION OF PYRIDINE BASES

Chemical and physical properties of the chief pyridine bases—diluting and distillation of pyridine acid—recovery of crude pyridine bases from pyridine water—details of an actual working—drying crude pyridine bases—rectifying dried crude pyridine bases—preparation of 90 per cent. at 140° C. pyridine bases and also heavy bases—yield of pyridine bases from coal tar light oils.

PYRIDINE bases as recovered from coal tar consist of a mixture of aromatic bases corresponding to the general formula CnH_2n-5N, of which the chief are pyridine, picolines, lutidines, and collidines.

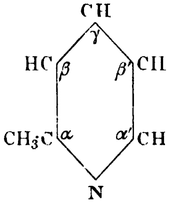
Pyridine, C_5H_5N, is a colourless, mobile liquid, possessing a peculiar unpleasant odour. Its specific gravity at 0° C. is 1.0033, at 15° C. 0.9855, and at 25° C. 0.976. It forms colourless crystals which melt at less than —100° C., and it boils at 116° C. (corr.). In water, alcohol, and ether it is soluble in all proportions, and it turns red litmus blue. Pyridine is represented by the following constitutional formula:—



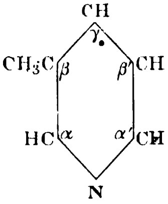
It is very stable towards oxidising agents such as nitric and chromic acids, even when boiling, and is only with difficulty attacked by the halogens. If heated to 330° C. with a mixture of concentrated nitric and sulphuric acids, β-nitro-pyridine is formed, in the shape of colourless, needle-like crystals possessing a melting-point of 41° C. and boiling at 216° C. Boiling with concentrated sulphuric acid yields a sulpho compound.

Pyridine is a strong tertiary base, and it forms crystalline salts with one equivalent of a mineral acid such as the sulphate, $(C_5H_5N)_2,H_2SO_4$, and the hydrochloride, C_5H_5N,HCl. With platinum chloride it forms a double salt, $(C_5H_5N,HCl)_2PtCl_4$, which crystallises in orange yellow needles, melting at 240° C. and dissolving with ease in water. On prolonged boiling this solution deposits a very sparingly soluble yellow salt of the formula $(C_5H_5N)_2PtCl_4$. Pyridine reacts with methyl iodide, forming pyridine methiodide, C_5H_5N,CH_3I, and, like ammonia, it blackens mercurous chloride. When pyridine is added to a solution of ferric chloride it gives a precipitate of ferric hydrate.

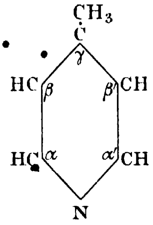
The three picolines or methyl pryidines, $CH_3.C_5H_4N$, possess many properties in common with pyridine. They are represented by the following constitutional formulæ:—



α-picoline.



β-picoline.



γ-picoline.

The first or α-picoline has a specific gravity of 0.9613 at 0° C. and of 0.9526 at 10° C. It boils at 133.5° C. (corr.), and is oxidised by potassium permanganate to picolinic acid, $C_5H_5N.\alpha COOH$. The β-picoline possesses a specific gravity of 0.9762 at 0° C., and it boils at 143.5° C. On oxidation it yields nicotinic acid, $C_5H_5N.\beta.COOH$. The last of these isomers, γ-picoline, has a specific gravity of 0.9742 at 0° C., it boils at 142.5-144.5° C., and on oxidising is converted into isonicotinic acid, $C_5H_5N.\gamma.COOH$.

There are six isomeric dimethyl pyridines or lutidines $(CH_3)_2C_5H_3N$, the chief of them being α α lutidine, having a specific gravity of 0.9467 at 0° C, and boiling at 156° C. (corr.); 2.4 lutidine, with a specific gravity of 0.9493 at 0° C. and a boiling-point of 157° C. (corr.), and 2.6 lutidine, possessing a specific gravity of 0.9420° at 0° C. and boiling at 142-143° C. (corr.).

The isomeric trimethyl pyridines or collidines are represented by the formula $C_5H_2(CH_3)_3N$; and 1 .3 .5 collidine possesses a specific gravity of 0.917 at 15° C., and it boils at 172° C. (corr.). The 1 .3 .4 isomer boils at 165-168° C. (corr.).

The pyridine acid as it is run off from the bottom of the washing tanks contains, in addition to pyridine bases, oily and resinous substances, and it is necessary to separate these substances before the pyridine can be recovered. This is done by adding clean water, with thorough stirring, and the amount added is, as a rule, about the same bulk as that of the pyridine acid. Some prefer to work to a specific gravity, and if this is done, it will vary between 40° and 45° Tw. It should be borne in mind that unless sufficient water is added, some of the oil and resinous matter may be retained in the pyridine acid, and if this does happen, the whole batch of crude pyridine will be spoilt. It is far better to slightly over, than under, dilute the pyridine acid. A point worth bearing in mind is that sometimes the first wash water (after the acid washes) from the benzol and naphtha may contain some pyridine bases, and therefore this water may be used with advantage to dilute the pyridine acid.

After the addition of the water, and a thorough stirring, the contents of the tank are allowed to rest for some hours. It is advisable, if it can possibly be managed, to allow the contents of the tank to rest overnight; the longer the period of rest, the more complete the separation of oily and resinous matters. When these substances have completely separated, they are skimmed off the subnatant clarified pyridine acid. Should the mass be heavy and resinous in nature, it is usually burned at the steam boilers. If, however, it is oily and will flow, it may be mixed with creosote oil, or if it appears to be composed to a large extent of unaltered benzene hydrocarbons, then it may be mixed with crude oils. If it is mixed with creosote or crude oils, care must be taken that no acid liquor is removed with it.

It is wise to submit a sample of pyridine acid to a test in the laboratory to see whether it is saturated with pyridine bases. If it is not, it may be used as a first wash on a fresh oil, after it has been diluted a little, and the oily and resinous matter skimmed off. By this means a further quantity of pyridine bases will be taken up and generally a complete saturation obtained, at the same time very little oily or resinous matter is picked up. Pyridine acid of this nature must, however, be put through the same process of dilution as that already described before working up for the recovery of bases.

A useful point to bear in mind is that the condensed water from a steam distillation of once-distilled light oil contains some pyridine bases. When it is convenient, this water should be used to dilute the pyridine acid. The following details of an actual distillation will illustrate this point:—

Once-distilled light oil charged into the still and submitted to distillation by steam, the volume being 1200 gallons.

Time.	Rate of distillation.		Pyridine bases in water.
	Water	Oil.	
Hour.	Gall. per hour.	Gall. per hour.	Per Cent.
1st	1	100	1.3
4th	25	75	1.5
9th	45	50	0.65
12th	55	20	trace

Volume of pyridine bases in the bulked water, 2.73 gallons.

Amount of pyridine bases removed from the oil by water, 0.228 per cent.

The clarified pyridine acid is run from the bottom of the diluting or treatment tank into the acid egg. In the meantime the still is charged with a quantity of quicklime. The quicklime is slaked while in the still, and the mass thoroughly boiled up with open steam, the manlid of course being closed prior to the boiling operation. When the lime-milk is thoroughly heated, the pyridine acid in the egg may be blown into the still. The pyridine acid should not, under any circumstances, be introduced into the still first, as owing to its more or less acid nature, it is apt to act upon the metal, and also as the reaction with lime commences at once, the addition of this material last will make the operation obnoxious and may result in some loss. It will generally be found that the distillation commences almost as soon as the contents of the egg have been discharged into the still, and on this account care must be taken when introducing open steam into the still, otherwise there is a risk of blowing over some of the contents into the coil and receiving tank. It must of course be remembered that the water flow through the condenser tank should be started before charging the pyridine acid on to the lime-milk. Immediately the acid egg is discharged it is advisable to open the drain cock and thoroughly drain, and then cleanse by blowing open steam into the egg for a short time.

The rate of distillation is controlled so that the distillate (which consists for some considerable part of the operation of a solution of pyridine bases in water) flows from the worm end in a stream about the thickness of three fingers placed together. This distillate should leave the condenser coil at the beginning perfectly clear, not cloudy. There are times when a slight cloudiness appears, which clears up in, say, about ten minutes. If, however, the cloudiness persists for any considerable length of time, then it is an indication that an excess of oily matter has got into the still with the pyridine acid. In a case like this, there is nothing to do but finish the distillation and recover the pyridine, as will be described shortly, dissolve it in dilute acid, and allow the oil to separate and then skim off, after which the clarified pyridine acid will have to be submitted to another distillation. Towards the end of the distillation, it will be noticed that the distillate leaves the worm end cloudy. This cloudiness is not due to oily material, but to heavy pyridine bases which are not soluble in water. These bases are worth recovering, but are not so valuble as the soluble ones, and the distillation is continued for some little time after the appearance of the cloudiness which indicates their presence. The best method of obtaining the point at which the distillation should be discontinued is to examine by a rough test a sample of the distillate as it leaves the worm end for the percentage of pyridine bases. This test is carried out as follows. Two hundred c.c.'s of the distillate are run into a separating funnel and "sprung" with about 80 c.c.'s of 90° Tw. caustic soda. After a short rest the under-lye is removed and a further quantity of 90° Tw. caustic soda (about 50 c.c.'s) added. The lot is well shaken, allowed to rest, the under-lye removed, and the bases run into a graduated measure.

If it is desired to recover all the heavy bases possible, then the distillation should cease when about ½ per cent. is present in the distillate; otherwise the operation is brought to a close when 1 per cent. of bases are present in the distillate as it runs from the worm end. The length of time which a still may run between 1 and ½ per cent. is sometimes considerable, and it may cost in many cases more for steam, etc., than the heavy bases which are recovered are worth. In addition to this, there is such a large volume of water distilling into the pyridine water tank that a very considerable amount of soda will be required to throw the whole of the pyridine bases up, and this will result in a very weak recovered caustic lye, which may require concentration before it can be used in the works for any other purpose. With further reference to this point, some distillers prefer to collect heavier bases in a separate tank and spring them separately with soda. Throughout the whole operation the distillate should leave the worm end at a temperature below 75° Fahr.

Details of an actual working will no doubt be of use to the student.

Charge of diluted and clarified pyridine acid into still, 350 gallons. Distillation commenced at 12 noon. Pyridine bases in distillate estimated with 90° Tw. caustic soda lye.

Time.	Percentage of bases in distillate at worm end.	Average rate of distillation.	Remarks.
12.15	56	110 gall. per hour	Heavy bases appeared at 1.30 p.m. At 3 p.m. 292 galls. of distillate collected. At 4 p.m. 400 galls. collected
12.30	48		
12.45	43		
1.00	31		
2.00	10		
3.00	4		
3.45	2		
4.00	1.2 =1.03 dried bases		

It is advisable to discharge the contents of the still through the gate valve at the bottom into the tank underneath very shortly after the operation of distillation is finished. If this is not done, there is a tendency for the lime residue (this consists chiefly of a mixture of calcium sulphate and unreacted-upon lime) to settle on to the still bottom and sides into a dense mass which is difficult to remove. As soon as possible after the discharge of the lime mud, the manhole should be opened and the sides and bottom of the still washed down with cold water. The mud, after draining by filtration or any other method found suitable in the works, is either taken to a "tip" or got rid of in any other convenient manner.

With reference to the quantity of lime required for a distillation of clarified pyridine acid, this will vary somewhat according to the amount of sulphates of the bases present. It is as well to submit a small quantity to an examination in the chemical laboratory for the amount of sulphuric acid, and then calculate the quantity of lime required for neutralisation. A slight excess over this quantity is generally added. As a guide 500 gallons of clarified pyridine acid, at a strength of about 40° Tw., will require 1600 lbs. of Buxton lime. The writer, however, strongly advises a laboratory test to be made each time, rather than working by rule of thumb.

The weak pyridine water in the receiver will contain a varying quantity of pyridine bases. Average amounts range between 35 and 40 per cent. This pyridine is recovered in most works by the addition of caustic soda of moderately high specific gravity. Pyridine bases are not soluble to any appreciable extent in solutions of caustic soda above 30° Tw. It is therefore necessary to use a strength of caustic soda sufficiently high to yield an under-lye of a strength not less than 30° Tw. or 1.15 specific gravity at 60° Fahr. A good strength to use for the separation or springing of the pyridine bases from the water is between 45° and 50° Tw. While adding the caustic soda lye, the contents of the tank should be thoroughly agitated, and when this operation is finished, a period of resting of, say, one or two hours should be allowed. The weak under-lye may then be run off into a storage tank for further use, say for the recovery of cresylic acid or phenols, or it may be concentrated or reinforced with solid caustic soda to raise its strength. The pyridine which has separated will yet contain water, and it is necessary on this account to dry it.

The pyridine bases are considered as sufficiently "dry" when they contain not more than 4 per cent. of water. The drying process may require several treatments with strong caustic soda, but in all cases the last operation should be conducted with a caustic soda lye of a strength of not less than 90° Tw. In the writer's opinion caustic soda for use in the drying operations should not be weaker than 60° Tw. for a commencement. It is not possible to give any definite figures in connection with the volume required to dry pyridine bases, but these quantities can be found quite easily by carrying out rough laboratory tests on a given quantity of the bases. If 50 c.c.'s are taken in a 100 c.c. test mixer, and small quantities of caustic soda of the strength it is desired to use are added, shaking after each addition and allowing to settle until a point is reached where a further addition of the caustic lye shows no further shrinkage of the pyridine bases, then from the amount of caustic soda required to reach this point the volume necessary to dry the bases contained in the treatment tank can be obtained by a simple calculation.

In a works where the CO_2 process for the recovery of phenols is in use, the pyridine may be conveniently sprung or separated from the water by the use of soda ash (58 per cent. alkali). It must be remembered, however, that the separated pyridine cannot be dried with this material. The under-lye of soda ash solution can be used for reinforcing the spent liquor (impure carbonate of soda solution) obtained from the reaction tower before it is causticised. (See Chapter viii, page 116).

This under-lye may also be causticised after diluting to a strength of about 23° Tw. and then used in the CO_2 process or else concentrated and used on the pyridine plant. The soda ash should be added in the dry state, and after each addition of, say, a couple of hundred pounds, the tank contents should be very thoroughly agitated. It is necessary to continue this agitation until the whole of the ash has dissolved, after which the contents are allowed to rest to enable the "sprung" pyridine to rise to the surface. The under-lye of soda ash solution is run off and any drainings removed before the addition of caustic soda for the purpose of drying.

With reference to the quantity of soda ash required to "spring" pyridine bases from weak pyridine water, the following figures may serve as a guide. To every 100 gallons of pyridine water, about 170 lbs. of 58 per cent. soda ash is added. The under-lye, after the separation of the pyridine bases, will test about 40° Tw. If soda ash is used for "springing," the drying operation is carried out in the manner already described.

The "springing" and drying operation may be carried out in the receiving tank, but it is advisable, especially in cases in which a large volume of pyridine acid is to be worked up, to carry out this series of operations in another tank. This will relieve the receiver, and a further distilling operation may be carried on within an hour or so of the finish of the previous one.

The dried pyridine may be run into a storage tank to await the process of rectification, or if this process is not carried out at the works, then the pyridine is generally filled into barrels, or, better still, into iron drums, ready for despatch. It is necessary of course to sell this material on a test, and the method of carrying this out will be found on page 232, chapter xix.

In the process of rectifying crude dried pyridine, it is a good policy to collect the fractions into small receivers or packages, so that each may be tested at the end of the operation, and a suitable mixing made to obtain a rectified pyridine which will answer any test required by the buyer. The two chief types of rectified pyridine are: one which will give not less than 90 per cent. at 140° C. when distilled in a 100 c.c. Wurtz flask, and the other which yields 50 per cent. up to 140, and 90 per cent. up to 160° C. There are other tests which these rectified pyridines are required to answer, and they will be described fully in chapter xix.

Having charged the still with a quantity of crude dried pyridine, the fire is lighted, and the temperature of the still contents raised fairly rapidly at first, but as soon as the dome begins to get hot the firing is carefully regulated until the distillate appears at the worm end. Priming into the fractionating column must be avoided.

The distillate is now collected until a sample taken from the worm end and tested does not commence to distil until 140° C. is reached. This fraction may be collected in a single receiver and reserved for 90 per cent. at 140° C. pyridine. If this is done it is advisable to test the contents of the receiver frequently for the percentage at 140° C., after a thorough mixing, when the change-over point is near at hand. The distillation is continued from the point just mentioned until a sample collected at the worm end and tested does not yield anything at 160° C. This fraction is known as heavy refined pyridine.

Another plan may be used for collecting the first fraction from the distillation of crude pyridine. It is to run the distillate into 40-50-gallon drums and cut for the first fraction when a sample taken from the drum into which the distillate is " working " and tested yields about 70 per cent. at 140° C. The second fraction is collected between this point and that at which a sample of the distillate when tested yields nothing at 160° C.

After the second fraction has been collected, distillation is discontinued, and the residue run to the bottoms tank, after an interval of an hour or so, in order to allow it to cool down somewhat. The second fraction is refractionated in the same, or a similar still, in order to obtain some more pyridine bases suitable for mixing with the first fraction. It is advisable to split this fraction on redistillation into two portions, cutting the first fraction when a sample from the worm end begins to distil at 140° C. and the second fraction when a sample tested from the worm end yields nothing at 160° C. The residue in the still is run to the bottoms tank. It is a good plan to collect these two fractions in carboys or small drums, as it renders it more convenient when carrying out the mixing process.

With reference to this process, it is not easy to describe in detail the method of carrying it out. It requires a few months' experience in order to decide correctly how many gallons of bases giving one test should be added to bases of another test to produce the desired result. It is a good plan to test the contents of the carboys obtained from the refractionation of the second fraction from the first distillation, and also the contents of the drums which contain the first fraction from the first distillation. Having obtained these distillation tests, experience will teach whether the contents of one or more carboys from the redistillation of the second fraction should be mixed with the first fraction, or whether any of the first fraction should be removed before the mixing is carried out. If it is found that the contents of any of the carboys or drums contain oil, or an excess of water, then they should be rejected for reworking. It is often possible to use pyridine bases containing a fair quantity of water, as the greater part of the distillate is generally free from this substance. If a little oil be present it is generally quite safe to employ for mixing, but it must be used with caution. In the finished pyridine, according to most specifications, water should not exceed 7 per cent., and, when tested according to usual specifications, should show no signs of oil. The methods of testing pyridine bases, both crude and rectified, will be described in chapter xix.

With reference to the bottoms, these are sometimes refractionated, and may yield 2 per cent. or 3 per cent. below 140° C. This of course is useful for mixing purposes. The distillation may now be carried on up to a point where a sample collected from the worm end and tested yields nothing at about 180° C., and this distillate can be sold as heavy bases. Sometimes the bottoms are sold under the same term without redistillation.

With reference to cleaning the still, it is policy to carry out this operation after every second distillation when working dried, crude pyridine, and after every distillation when working bottoms or heavy bases.

The following details referring to the yield of pyridine bases from once distilled naphtha and once distilled benzol will no doubt be instructive. The figures are average ones only, and it must be remembered that distillates from different tars will give results higher or lower than them.

Once distilled benzol. 1100 gallons taken.

One wash only.
Pyridine bases recovered :— Per cent.
8.27 gallons 90 per cent. at 140° C. pyridine bases =0.75
0.63 gallons higher bases =0.057

Once distilled naphtha. 1550 gallons taken.

1st wash.
29.7 gallons 90 per cent. at 140° C. pyridine bases.
8.3 ,, higher bases.
2nd wash.
28.3 gallons 90 per cent. at 140° C. pyridine bases.
8.9 ,, higher bases.
3rd wash.
4.2 gallons 90 per cent. at 140° C. pyridine bases.
1.3 ,, higher bases.
Total. Per cent.
62.2 gallons 90 per cent. at 140° C. pyridine bases =4.01
18.5 ,, higher bases. = 1.19

An average amount of crude pyridine obtained per ton of tar distilled is 0.247 gallons.

CHAPTER XIV

PLANT FOR THE MANUFACTURE OF CRUDE NAPHTHALENE AND ANTHRACENE

Salting-out tanks—recrystallising tanks—hydraulic presses—centrifugal machine—anthracene oil still—crystallising tanks—hydraulic press—filter press—grinding machinery—washing tank.

CRUDE naphthalene and anthracene are not prepared in all tar distilleries, and this remark applies especially to the latter product. It is thought advisable, however, to deal with the subject briefly in this and the next chapter. Crude naphthalene is placed on the market chiefly in three qualities, viz.: drained, pressed, and "whizzed"; and the pieces of plant necessary for the production of these qualities are as follows: Salting-out tanks or boilers, recrystallising tanks, hydraulic presses, centrifugal machines, together with the necessary steam piping, bags, staging, etc.

The salting-out tanks or boilers may be of any convenient shape. Usually they are second-hand steam boilers with the tubes drawn and the ends blanked, or else second-hand egg-ended steam boilers. The size of these tanks or boilers varies generally between 4000 and 10,000 gallons. Each tank should be provided with a 2-inch inlet pipe; one 2-inch outlet pipe with tap placed at the bottom for the purpose of draining, the outlet being closed inside by means of a lead-lined plug with a long handle, to prevent it getting salted up (this pipe may be connected to a pump if desired, or else arranged to lead the liquid oil into storage tanks by force of gravity); a suitable closed steam coil, built up of 1½-inch steam-pipe; a manhole of the usual size and provided with a loose cover; and also a 2-inch outlet pipe and tap, which may be placed at the bottom of the tank for the removal of the melted salts. Some prefer to put in a by-pass on the draining pipe, and use this for the removal of the melted salts. Others prefer to insert through the top of the boiler a suction pipe reaching to the bottom for the same purpose. Neither of these plans is good. The outlet pipe for the melted salts is connected up to a steam pump, and a pipe line is arranged from the delivery side of the pump, so that the liquid may be delivered into the recrystallising tanks. Reducing T's should be placed on the suction and delivery mains, and connected up to a 1-inch steam-pipe, so that steam may be blown through the pipes after the pumping operation, in order to thoroughly clean them and prevent them becoming salted up or choked. The number of salting-out tanks or boilers required will vary of course according to the quantity of salty oil it is desired to deal with per day.

Tanks for recrystallising the melted salts should be shallow. A general size is 8 feet wide, 14 feet long, and 2 feet deep. The tanks may be placed on the ground level, or, better, a foot or two above the same, as this will allow air to circulate round them. They are provided with one or more inch outlet pipes and taps, by which to drain away the mother liquor or oil which separates into underground tanks or boilers. The outlet holes should be closed by means of lead-lined plugs, with a handle to facilitate their removal. These tanks must of course be under cover, and it is an advantage to arrange that the room in which they are placed can be suitably cooled, or else the tanks themselves may be artificially chilled during hot weather. It may be added that many works do not trouble about chilling at all, but recover just so much salts as will crystallise out at the temperature existing during the time of working.

The salts from the recrystallising tank are removed by manual labour, and either pressed in hydraulic presses or dealt with in a centrifugal machine. Suitable types of hydraulic press are shown in Figs. 64 and 65. The head, bottom, and table of these presses are of the best cast-iron, machined where necessary. Close-grained cast-iron is used for the ram, and it is polished the full length to fit the cylinder, which is constructed of best cast steel and supplied with a steel gland. The columns are made of mild steel and fitted with steel nuts. Division plates of mild steel are supplied loose or as part of the press, as shown in Fig. 65. Centrifugal machines are specially made for this purpose by several firms, and an excellent type is illustrated in Fig. 66. This machine is electrically driven and suspended on three pillars so arranged that the vibration is absorbed and the necessity for a massive foundation done away with. It is self-contained, the electric motor being built on to the centre spindle. The electric motor is fitted with an automatic starting-gear, which makes the machine fool proof, and the starting up quite automatic. An outlet is provided in the revolving basket through which the "whizzed" material can be discharged down the discharge shoot and on to a small truck or barrow, or into a sack placed underneath. Steam-driven machines are sometimes employed instead of electrically driven ones. It is of course necessary to provide an underground tank into which the oil pressed out during the application of hydraulic pressure, or separated by centrifugal force in the "whizzing" operation, can be run.

The methods of working up crude anthracene vary: some prefer to redistil the green oil, others simply to allow it to cool and separate out the crude anthracene. If it is desired to distil the oil before treatment, then it is necessary to put in a still of wrought-iron or mild steel, somewhat similar to a tar still in shape, and provided with similar fittings, such as charge-pipe, outlet pipe, swan neck and stool, safety-valve, manhole and lid, etc. The still bottom should not be built with very much rise, the crown plate having a rise of between 12 inches and 18 inches. The concave portion of the bottom is connected to channel plates, as already described under tar stills, and the dome of the still should have a rise of between 12 inches and 14 inches, according to the size of the still. It is of course necessary to connect the still to a condenser coil, which latter

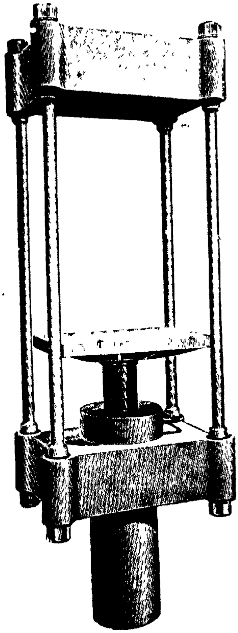


FIG. 64.—Hydraulic Press.

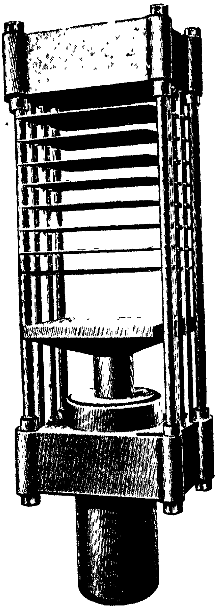


FIG. 65.—Hydraulic Press.

piece of apparatus will require the usual condenser tank, fitted in all respects as described under tar or light oil stills. The number of receivers will vary according to the desire to separate the distillate into one, two, or three fractions. Whether the green oil or anthracene oil is distilled or not, the remainder of the plant is practically the same. It consists chiefly of shallow, crystallising tanks, about the same size as those used for the recrystallisation of the naphthalene, a filter press or presses,

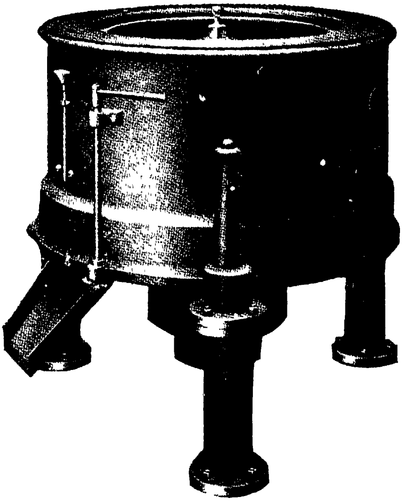


Fig. 66.—Centrifugal Machine.

washing tanks, one or more hydraulic presses, and an edge runner or other suitable mill for grinding the washed and re-pressed anthracene. The crystallising tanks are fitted up with 2-inch pipes and taps at the bottom for the purpose of draining. They should of course be under cover, and sometimes the chamber in which they are erected is artificially cooled during the summer months. As a matter of fact the arrangement of these tanks and their fittings is very similar to that already described under naphthalene recrystallising tanks.

If it is desired to press the crude anthracene or crude naphthalene at an elevated temperature, then a horizontal or vertical hydraulic hot press must be installed. In the best types of hot press each division plate is connected to a flexible steam-pipe and so constructed that steam may circulate in its interior. An excellent type of filter press is illustrated in Fig. 67. For dealing with anthracene this piece of apparatus is usually made with very deep chambers and of the flush plate and distance frame type. The plates may be either circular or square in shape, and are fitted with plain bib outlets for the filtrate. With reference to the feed inlet, this can be arranged (*a*) through a passage in one corner of each plate having a port to each distance frame, and (*b*) by a central hole through the plates. In order to secure the maximum amount of area of cloth available for effective filtration, careful attention must be given to the construction of the plates. The plates of the press illustrated have their faces studded with small, truncated, square pyramids; and this in the writer's opinion forms the most efficient support for the filter cloths.

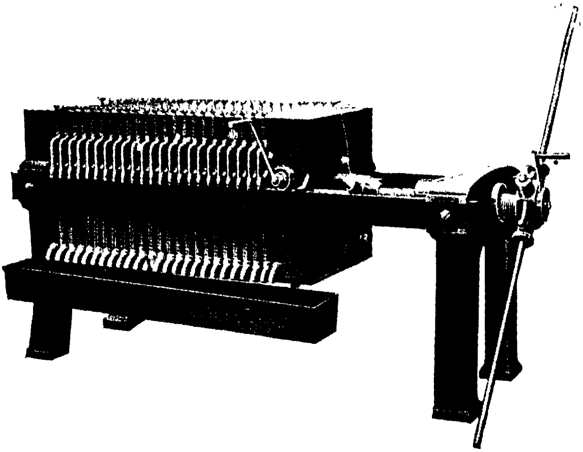


FIG. 67.—Filter Press.

With reference to grinding machinery, one of the many types of edge runner may be used, or a Carr's disintegrator, or other suitable type.

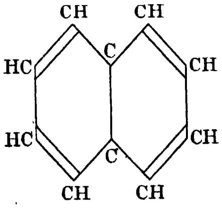
Tanks for washing the anthracene are constructed of wrought-iron or mild steel and provided with paddle or archimedean screw agitators. They may be erected in a vertical or horizontal position, and should in either case be covered in. The washer should be fitted with a closed steam coil in order to warm up the charge, a charge-pipe for introducing the washing material, a manhole about 18 inches by 12 inches, through which the pressed anthracene may be dropped, and an outlet pipe to remove the contents after washing to the filter press.

CHAPTER XV

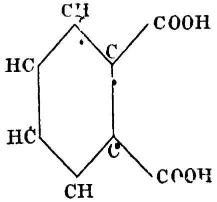
THE MANUFACTURE OF CRUDE NAPHTHALENE AND ANTHRACENE

Chemical and physical properties of naphthalene and anthracene—salting-out the oils—recrystallising the naphthalene salts—"drained" naphthalene—"whizzed," naphthalene—"pressed" naphthalene—distillation of anthracene oil—"salting-out" the oil—filtering the "salted-out" oil—pressing and washing crude anthracene.

NAPHTHALENE, $C_{10}H_8$, occurs in the form of white monoclinic crystals possessing a peculiar tar-like odour. Its specific gravity at 15° C. is 1.1517 and at 100° C. 0.9628. Naphthalene melts at 80° C. (corr.) and boils at 218.21° C. (corr.). In cold water it is quite insoluble, but it is very slightly soluble in hot water. It is dissolved by ether, alcohol, chloroform, carbon disulphide, acetic acid and the essential oils. Toluene and benzene also dissolve naphthalene. At 15° C. 100 c.c. of alcohol dissolve 5.29 parts of naphthalene and at 16.5° C. 31.94 parts are dissolved by 100 pars of toluene. It is represented by the following constitutional formula :—



Naphthalene is a very stable substance and is converted into simpler substances with great difficulty. If it is boiled with dilute chromic or nitric acid it is slowly oxidised into ortho-phthalic acid :—

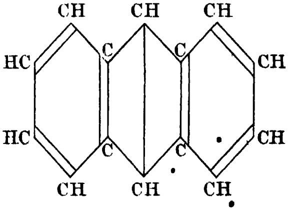


It is readily acted upon by concentrated nitric acid, forming nitro derivatives, the reaction being facilitated by the presence of concentrated sulphuric acid. If it is heated with concentrated sulphuric acid naphthalene is readily sulphonated, forming naphthalene sulphonic acids.

On adding a cold alcoholic solution of picric acid to a cold alcoholic solution of naphthalene a yellow crystalline precipitate of naphthalene picrate, $C_{10}H_8.C_6H_2(NO_2)_3.OH$, is formed which melts at 149° C.

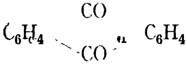
Anthracene, $C_6H_4 : (CH)_2 : C_6H_4$, in the pure state occurs in the form of small white glistening plates with a violet fluorescence. It has a specific gravity of 1.147, melts at 216.5° C. (corr.), and boils at 351° C. (corr). In water it is insoluble, but is dissolved by alcohol, ether, benzene, carbon disulphide and many other organic solvents. At 15° C. 100 parts of alcohol dissolve 0.59 part of anthracene. In ether it is rather more soluble, 100 parts dissolving 1.17 parts at 15° C.

The constitutional formula of anthracene is written thus :—



If anthracene is exposed to light it is transformed into dianthracene, which in the dark becomes depolymerised to anthracene. This is one of the rare instances of a reversible photochemical reaction.

$$2\ C_{14}H_{10} \xrightleftharpoons[\text{dark}]{\text{light}} C_{28}H_{20}.$$

It is not possible to nitrate anthracene, and when it is acted upon by nitric acid (and also chromic acid) it is oxidised to anthroquinone  $C_6H_4 \begin{matrix} CO \\ CO \end{matrix} C_6H_4$, which melts at 277° C.

When saturated alcoholic solutions of anthracene and picric acid are mixed, ruby-red needles of anthracene picrate, $C_{14}H_{10}.C_6H_2(NO_2)_3.OH$, are precipitated. These crystals melt at 138° C.

In the manufacture of crude naphthalene, washed light creosote, and also the bottoms from the benzol, naphtha and light oil stills are employed. It is necessary to see that the distillates, such as light creosote, are quite free from tarry matter if they are intended for this purpose. These oils are pumped into the crystallising boilers and allowed to remain for several days in order to crystallise out the naphthalene or "salts." The period of time which the contents of these boilers are allowed to rest will vary according to the time of the year and average out between three to five days. When the "salting-out" is completed, the oil which has separated is drained away through the drain-pipes into storage tanks. This oil is tested for its specific gravity, and if found to be low, is mixed with liquid heavier creosotes, or strained green oil, and placed upon the market as liquid creosote. The crude naphthalene remaining in the boilers is melted up by the aid of closed steam, and when the whole of it is in the liquid state, and at a temperature well above the crystallising point, it is pumped from the boilers into the recrystallising tanks. Immediately the pumping operation is finished, steam should be blown through the suction and delivery mains, in order to clear them of any liquid salts which may remain and which will, if not removed, solidify in the pipes and cause no end of trouble.

The liquid crude naphthalene in the recrystallising tanks is allowed to cool down and recrystallise out from the oil which has been carried over from the "salting-out" boilers. After a period, varying from two to four days, the drain taps are opened to allow any oil which has separated to run off. This oil is removed to storage boilers or tanks, and allowed to rest for several days, after which it is mixed with other liquid creosote oils and disposed of as liquid creosote. It may be added that any "salts" which is deposited in these boilers is melted up from time to time and pumped into the recrystallising tanks. After the crude naphthalene has thoroughly drained it may be placed into barrels or other suitable packages and disposed of as drained naphthalene.

If, however, it is desired to prepare from the drained naphthalene a quality known as "whizzed" naphthalene, it is removed from the recrystallizing tanks and charged into centrifugal machines. Care must be taken to level the "salts" in the cage of the machine, otherwise there is a great risk of wobbling, which may lead to an accident when the machine is set in motion. The cage should not be overcharged, and should not be started up too suddenly. With a good centrifugal, it is possible to "whiz" four to six charges per hour, the size of the charge of course varying according to the dimensions of the centrifugal. Should the centrifugal be self-discharging, then the "whizzed" crude naphthalene may be released from the bottom into a special receiving pan, or direct into sacks. The oil as it flows from the machine is conducted into the liquid creosote storage tanks or boilers.

Pressed naphthalene is prepared by taking the recrystallised crude from the recrystallising tanks and placing them into press bags. These bags are made of various materials, sometimes even ordinary sacking being used. The size of a bag when filled will vary according to the dimensions of the press, but an average may be taken as 9 inches wide, 18 inches long, and 3 inches thick. Care must be taken to keep the thickness of the filled bags as even as possible, otherwise there is a risk of rupturing the press table during the process of pressing. When charging, the press table is run down to the floor of the press. It is then covered with bags, arranged so that there is a space of about 2 inches between each. When the table is full, a wrought-iron plate about ¼ inch thick is placed upon the top of them, and this is covered with bags in a similar manner to the table. This operation is carried out until the press is charged. It is important that care be taken to arrange the plates and the bags on them so that they just cover one another, and do not project on any side. Any unevenness vertically will produce what is known as "shunting," *i.e.*, the middle will bulge out on one side or the other. This will not only produce some half-pressed material, but there is a very great risk of the press table fracturing. In some types of hydraulic press the plates are suspended from the press-head by steel links, and when the press is run down this results in the plates being of sufficient distance apart to charge with filled bags. If a press of this kind is used, it is necessary to place the bags on each plate so that they cover those on the plate immediately underneath.

When the operation of charging is completed, hydraulic pressure is applied, and the press gently run up. The pressure is then slowly increased until it indicates between 1½ to 2 tons to the square inch. After an interval of about one hour, the hydraulic pressure is released and the press discharged. On opening the bags and removing the pressed cakes, should any wet edges be noticed, these are cut off and re-pressed with another batch. The cakes of pressed naphthalene are now charged into a disentegrating machine, and when thoroughly broken up, placed into packages for dispatch.

A far better quality of pressed crude naphthalene is obtained by using a steam-heated hydrualic press and carrying out the process known as "hot pressing." A naphthalene which has been properly hot pressed will give very little trouble in the refining process and will yield an excellent finished product. It is very necessary to pay attention to the regulation of the temperature employed for pressing. Within limits the higher this temperature the better the result, as more foreign matter is removed, but it must not be forgotten that the presence of oil in the unpressed naphthalene lowers the melting point and if the naphthalene has not been carefully centrifugalled to remove the maximum amount of oil and a high temperature is employed during the pressing, then an excessive quantity of naphthalene will come away with the press drainings. It is advisable to let the works chemist determine the best temperature at which to press any individual working of naphthalene.

In the preparation of crude anthracene, if it is desired to redistil the anthracene oil as obtained direct from coal tar, then a quantity of this is charged into a still and the fraction which comes over between the point at which the distillate tests 14° Tw. at 60° Fahr. and that at which it tests 26° Tw. at 60° Fahr., or when it shows what is termed "grease," collected for this purpose. These figures are only approximate, and have to be varied according to the nature of the oil under treatment. It is rather difficult to explain what is meant by "grease." The distiller, by experience, is enabled to tell from the appearance of the distillate, if a small portion is allowed to cool on a piece of iron or glass plate, when anthracene approximately ceases and higher solid bodies appear. The presence of anthracene in the oil is generally shown by a curdy or gritty appearance when the oil is chilled, and "grease" when the oil on cooling sets to a buttery-like mess. The anthracene fraction is pumped into the crystallising tanks situated in the press house, and there allowed to cool in order to separate out the crude anthracene.

Should it be desired not to redistil the anthracene oil fraction as obtained from the tar stills, this is pumped from the receiver into the crystallising tanks, and is submitted to the same process as the redistilled "green oil" fraction. The length of time which the contents of the crystallising tanks have to rest in order to complete crystallisation will vary according to the time of the year, unless the chamber or the tanks are artificially cooled. From two to five days may be taken as averages throughout the year.

After the separation of the crude anthracene has taken place, the contents of the tanks are pumped through filter presses, or else into bag filters, which are prepared by tying special bagging over flanges fitted into the pumping main, and then fastening up the bottoms with cord, the lot being suspended over a tank to catch the drainings; or else into an ordinary filter tank across which is suspended a filter bed made of filter cloth or bagging, and supported by wicker or basket ware. At the present day the filter press is generally used, as it deals with the material most expeditiously. In pumping through a filter press, the pressure must be raised gradually and kept as long as possible at a low point. When the press is full and oil ceases to run from the press plates the press is opened and the cakes of filtered anthracene are removed. The filtrate, whichever way obtained, is known in the trade as strained or dead oil. The cakes from the filter-press may be submitted to pressure in a hydraulic press, and then ground up and washed, or else washed first, and after a further filtering pressed by hydraulic pressure, according to the quality of crude anthracene it is desired to produce. If it is required to press first, the cakes are broken up and charged into bags and then into the press, and then submitted to hydraulic pressure in a similar manner to that described under naphthalene. Sometimes the crude anthracene from the filter is passed through a centrifugal machine before submitting to hydraulic pressure. The filtered material is filled into bags and these are packed into the cage of the centrifugal, or if a suitable gauze is fitted to the cage, the crude anthracene may be charged into it direct. Often hydraulic pressure is applied at an elevated temperature. This is carried out by employing a steam-heated hydraulic press.

After the pressing operation is completed, the cakes are removed from the bags, ground up under an edge-runner or in a disintegrator, charged into the washer and washed with "salted out" (liquid) light creosote or a moderately heavy naphtha free from naphthalene. The quantity of liquid used to wash say one ton of pressed anthracene is about 500 to 600 gallons. When the washer is charged, the contents are heated up by the aid of closed steam and thoroughly well agitated. While washing a temperature of about 80° C. is maintained. The period of agitation varies according to individual ideas, but averages about three hours. After the washing operation, the contents of the washer are allowed to cool down to about 20° C. and then pumped through a filter press, the press cakes removed, and either hydraulically pressed, ground up, and spread out to dry in a drying room, or else roughly broken up as removed from the filter press and dried. The more complete the separation of the washing liquid from the crude anthracene, the purer the product; so if circumstances allow, it is far better to hydraulically press after the filter pressing operation than to dry after removing from the filter press. A point worth bearing in mind is that the same kind of oil should be used for the washing of all batches of anthracene, should it be desired to produce the same quality of this material.

CHAPTER XVI

PITCH AND PITCH "GETTING"

Soft pitch—medium hard and hard pitch—depth to run pitch in bay—cooling of pitch—protection of pitch-getter's eyes—"getting" or digging pitch—tools—cost of getting pitch—pitch cancer.

THERE are three chief grades of pitch, viz.: soft, medium and hard. These grades are distinguished from one another by what is known as their "twisting" or softening point. This point will vary somewhat according to the method used to obtain it: for soft pitch the average is about 110° Fahr., for medium pitch 140° Fahr., and for hard pitch 210° Fahr. At the present day a very large amount of pitch is purchased on the amount of volatile matter which it contains. The methods of conducting these tests are fully described in chapter xix.

With reference to soft pitch, this is not made in very large quantities, and when it is, it is generally filled into barrels, when sufficiently cool, instead of running on to a bay. It is a matter of impossibility to dig or "get" this pitch during the summer months. By far the largest quantity of pitch made is of the medium hard quality, and this, or the grade known as hard pitch, is run from the pitch coolers on to the bay, which is prepared as described in chapter vi, page 78. It is advisable not to run the pitch to too great a depth, the best thickness being between 15 inches to 18 inches. This depth of pitch will cool rapidly and is dug with a minimum of labour by the pitch-getters. With reference to the length of time that the pitch must remain on the bay before it can be "got," this will vary, naturally, according to the temperature of the atmosphere and the situation of the pitch bay. Under favourable conditions 24 to 36 hours is all that is necessary, but there are times when two or four days must elapse before pitch can be worked.

During the summer months it is advisable to get the pitch at night, or in the early hours of the morning, rather than during the hottest part of the day; and in order to keep the pitch cool, especially that portion which cannot be worked immediately, the surface should be covered with a thin layer of lime wash. This will prevent the absorption of the sun's rays during the daytime. If it is necessary for the men to work pitch which has been lime-washed on the surface, during the daytime, especially while the sun is shining upon it, the portion on which they are working should be washed with water and a hard brush to remove the lime-wash, as otherwise the glare will injure the men's eyes.

It is a general practice among pitch-getters, in order to protect the eyes, to wear a piece of black crêpe over them. This is not an efficient method of protecting these organs, as sometimes rather large particles of pitch will fly up from the bed, and will easily damage the eye in spite of the crêpe. Goggles made of fine copper wire gauze of between 30 to 40 meshes to the inch are much more suitable for this purpose, as the gauze will offer a considerable amount of resistance to flying pieces of pitch. It should be added that the workmen do not care about wearing goggles, and in many cases will not even wear crêpe. However, the management should insist upon this means of protection as a precaution against claims under the Workmen's Compensation Act. A good plan in order to prevent excessive rising of dust is to wet the pitch at the point where it is being dug, and often the workmen will carry this precaution out without being told.

Pitch is "got" by driving metal wedges into the layer on the bay with sledge-hammers weighing about 10 to 14 lbs. This breaks off large pieces, which are further broken down by the aid of pickaxes. The pitch is then shovelled into barrows or iron skips, according to the situation of the bed or the manner adopted by the management for loading trucks or carts. Sometimes the pitch bay is so situated that carts can be backed into it, and loaded direct by throwing the pitch into them with a shovel. If the bay is below the ground level, then it is necessary either to wheel the pitch in barrows up barrow-runs, or else to raise it skips in by means of a crane. Should the pitch bay be above the level of the railway trucks, then it is quite a simple matter to wheel the pitch in barrows from the point where it is being "got" and tip it into the trucks at the end of the run.

With reference to wedges, these must be made of good steel, about 2 feet 6 inches long and 1½ inches by 1½ inches in section; "set temper" steel is a very suitable grade to use. New wedges should be tough but not brittle, as the tendency seems to be for the steel to become very brittle in time, owing to repeated hammering and to the presence of fine pitch dust, which settles upon the head of the wedge. Brittle wedges are dangerous, as particles fly off and often cause accidents by cutting the "getter" about the body. The same remark applies to the hammers. Sledge-hammers having two faces are the best type to use, and the average workman prefers one of about 10 lbs. in weight.

The cost of "getting" pitch and loading it into wagons will vary somewhat for each works, according to the position of the pitch bay, the thickness of the pitch on the bay, the time of the year, and so on. Under normal conditions in a properly arranged and well managed works it will vary between 6d. and 7½d. per ton, including repairs. The average cost of repairs should work out at ¼d. per ton.

For many years it has been known that certain men engaged in the handling of pitch (and also anthracene) develop warty growths. These growths often ulcerate, and at times render it necessary to remove, by surgical treatment, the affected part. A year or two back a special inquiry was made at the instigation of the Home Office into this question, and it was discovered that these ulcerated warty growths occasionally become the seat of what is termed by medical men epitheliomatous cancer. This form of cancer is considered to be the least malignant, and if removed is not usually followed by a recurrence. Draft regulations were drawn up, and in the course of time objections were raised against these. Among the draft regulations, it was suggested that bathing and washing on the factory premises should be carried out. It was required that the workman should take a bath at the works at least every alternate weekday, and wash before leaving the works for meals, or at the end of the day, when a bath is not taken. One of the chief objections raised against these regulations was that of washing and bathing, the workmen stating that the application of water to the skin after pitch-getting caused them a considerable amount of pain. Owing to this and other objections a Home Office inquiry was made to consider the same, and an interesting pamphlet was published dealing with the results of the inquiry.[1]

It appears that pitch dust also causes severe inflammation of the conjunctival membrane and cornea of the eye, and in some cases may result in the formation of epithelimatous cancer on these membranes. In any case there is great danger of septic inflammation being set up, owing to bacteria getting into the ulceration, and the possible chance of the loss of sight. The wearing of goggles or crêpe will not prevent the fine pitch dust from getting into the eyes, and on this account it is advisable to wet the pitch somewhat at the point of working, as already stated, in order to prevent as far as possible the rising of dust during the "getting" operation.

The pamphlet just mentioned does not state what is the actual cause of the irritation, although it seems to point to the fact that the cause is two or more of several chemical substances contained in the pitch (or crude anthracene). These substances are divided into two groups: the *auxetics* (excitors of reproduction) which stimulate cell multiplication and *kinetics* (or augmentors) which increase the action of the auxetics. It appears that pitch cancer cannot be produced unless an auxetic and a kinetic are present. The auxetics appear to be bodies akin to the amido acids or their derivatives and the amines, and the kinetics substances of the ptomaine class, such as cadaverine and choline.

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[1] *The Problem of the Gas Works Pitch Industries and Cancer.* John Murray, Albemarle Street, London, W.1. Price 6d.

The writer made some experiments a while ago and was able to isolate small quantities of acridene from coal tar pitch, and, on making a few experiments with this material, found that it set up considerable irritation, particularly when applied to mucus membrane and especially when wetted. Possibly acridene is one of the hurtful substances of the auxetic type, but it rests with the medical men carrying out the inquiry to settle such a matter as this.

Several methods have been suggested for the removal from coal tar of the substances which induce cancer, and among them are those of H. W. Robinson and H. C. Ross.

Robinson's methods are briefly as follows: British Pats. 4159 and 10156, Feb. 8th and April 30th, 1913. The addition of small quantities of formaldehyde or other aldehyde to coal tar at a suitable stage in the distillation process results in a pitch entirely or almost free from auxetics and, therefore, harmless as regards liability to induce pitch cancer. Sugar or other substance which decomposes at a temperature below 250° C. with the formation of an aldehyde may be used. If formaldehyde is used it is added along with the steam after removing from the tar all the fractions which come over before anthracene oil. The quantity recommended is 1½ gallons of 40 per cent. formaldehyde for each 2000 gallons of tar.

Robinson: British Pat. 20767, Sep. 15th, 1913. Tar is treated for 60 to 90 minutes with ozonised air applied at a pressure of 20 to 30 lbs. per square inch.

Ross suggests the following: British Pat. 11984, Mar. 22, 1913. The auxetics in tar are removed by bringing the tar into intimate contact and spraying it with hot water or hot dilute acid. The mixture is projected on to a plate or plates to bring about a finely divided state, after which it is allowed to stand to separate the aqueous liquid or is treated by any other suitable process to attain this end. If hot water at a temperature between 100° to 212° Fahr. is employed then a volume twice that of the tar is taken, and if dilute acid is used, a volume one-half that of the tar will suffice. Sulphuric or hydrochloric acid of 5 per cent. strength is recommended.

CHAPTER XVII

CREOSOTE

Variation in specific gravity, distilling range, etc.—Wells' oil—fuel oil—sheep dip creosote—creosote for the manufacture of greases—creosote for the manufacture of black varnish—creosote for timber preservation—requirements of several specifications—creosote for the benzol recovery process—storage of creosote—volatility of creosote.

THE term creosote is used very broadly in the commercial world, and under it are often included oil-gas tar creosote, wood-tar creosote, coke-oven creosote, blast-furnace oil creosote, and several others. In this chapter it is intended to deal with coal tar creosote only.

Coal tar creosote as put on the market varies within fairly wide limits as regards specific gravity, content of phenols and naphthalene and distilling range. The gravity may vary between 1.000 and 1.070. Occasionally samples are met with a little lower in gravity, and sometimes higher. With reference to the percentage of tar acids, creosotes are sold containing but a mere trace up to about 25 per cent., and with regard to the percentage of naphthalene, this varies very considerably, some creosotes containing 30 per cent. and even more, others but mere traces. Some idea of the variation in distilling range will be obtained by referring to Table XX.

TABLE XX

From drop to 200°	From drop to 250° C.	From drop to 300° C.	Residue.
Per cent.	Per cent	Per cent.	Per cent.
0 to 16	25 to 75	63 to 85	5 to 35

Creosotes as obtained direct from coal tar by distillation differ somewhat according to the quality of the tar, and more often than not are put through a special treatment, *i.e.*, removing a certain portion of the tar acids or naphthalene or submitting to a redistillation, before placing on the market. More frequently, owing to the fact that most buyers require creosote to answer their own specification, blends of various grades have to be made. A creosote required for burning, say, in a Wells lamp must be quite free from dirt and naphthalene. As a matter of fact it should not deposit "salts" (or naphthalene) at a temperature of 40° Fahr. after exposure to that temperature for six hours. The average specific gravity for creosote for this purpose is 1.050-1.060 at 60° Fahr., and it should not contain more than 2 per cent. of water when tested by distillation.

Creosote oil if properly prepared makes a fairly good fuel oil when compared with petroleum fuel oils such as American residuum, Russian ostatki, and shale oil. Much care must, however, be employed in the preparation, otherwise troubles will result when it comes to be burned. It is necessary to use a heavy creosote or, better still, an anthracene oil for fuel purposes, and it must be free from any kind of solid matter, such as that of an earthy, carbonaceous or fibrous nature, and also from naphthalene or anthracene salts. All these bodies will choke the orifices of the nozzles of the burners, and naphthalene or anthracene salts will also choke up the supply pipes in the cold weather. It has also been found that these "salts" form a crust round the mouths of the burners. Fuel oil must not deposit any naphthalene or anthracene salts when cooled to 0° C. and kept at that temperature for 24 hours. It must be quite free from water, as the presence of this material will probably cause the flame to go out, and if this is not noticed a disastrous explosion may take place in the furnace, owing to the oil spray and air forming an explosive mixture. Not more than 0.5 per cent. of water, determined by distillation, should be allowed. The flash point must not be low, the minimum being 150° C. Abel's close test. Creosote will, if properly prepared, test above 210° C. Abel's close test. Creosote fuel oil, if burned with care in regard to air supply, will give excellent results and smoke troubles need not be feared. The calorific power of this type of fuel oil varies more or less between 16,200 and 17,500 British thermal units per lb. For purposes of comparison the figures given in Table XXI will prove of use.

TABLE XXI

Kind of Fuel Oil.	Specific Gravity.	Flash Point ° F.	Calorific value by bomb. per lb.		Actual Evaporative Power in Practice from and at 212° F. lbs.
			Calories.	B.Th.U.	
Heavy tar oil	1.084	218	8,916	16,050	12.0
Blast-furnace oil	0.979	206	8,933	16,080	12.0
American residuum	0.886	350	10,904	19,627	15.0
Russian ostatki	0.956	308	10,800	19,440	14.8
Shale oil	0.875	288	10,120	18,217	13.8

Creosote oils intended for the manufacture of sheep dips and disinfectant fluids must be specially prepared if the best results are desired. One of the chief points to bear in mind is the removal of naphthalene "salts." The presence of this substance has a very deleterious effect on the emulsifying power of the finished dip or disinfectant. It is one of the causes of "falling heavy," *i.e.*, on addition to water, falling through the water to the bottom of the vessel instead of spreading in the form of white clouds. Naphthalene "salts" should be separated very carefully by allowing the creosote to stand a considerable time during the cold weather or, far better still, by refrigeration Some of the creosote oils obtained from the naphthalene plant prove useful in this respect.

All creosotes intended for the purpose now under consideration must contain a certain percentage of tar acids, this varying according to the requirements of the buyer. Some buyers require 3 per cent., others 5, 10, 15, 20 per cent. or more. It should be mentioned that redistilled creosote is the most suitable for sheep dip and disinfectant manufacture. Another matter for consideration is the specific gravity of the creosote. The best results are obtained, as a general rule, if the oils are of a specific gravity approaching that of water. This means that the lighter the specific gravity of the creosote the better the emulsifying power of the fluid, other things being equal. Naturally, it is not always possible to obtain a coal tar creosote of a specific gravity of 1.000 and in any case never in large quantities, but it is possible to make a blend of a creosote, say, of specific gravity 1.055 or even of a higher or lower gravity with a fairly high distilling petroleum, say, of a specific gravity between 0.800 and 0.820. The specific gravity of the finished disinfectant fluid or sheep dip will, of course, be greater than that of water, but it must be remembered that the soap used in the preparation "dissolves" in the water, to which the fluid is added prior to being used, while the oils do not. The function of the soap in the fluid is to form a colloidal solution with water which will emulsify the oily portion of the disinfectant and keep it suspended in a very finely divided state. Other things being equal the finer the state of the emulsion the more efficient is the action of the disinfectant fluid.

In the manufacture of the cheaper fluids rosin soap is used alone but in the higher quality disinfectants a mixture of rosin soap with a vegetable oil soap, or a vegetable oil soap alone, is employed. The chief vegetable oils employed are castor oil and linseed oil, or their fatty acids. It must be remembered that excess of caustic alkali(caustic soda or potash) is to be avoided; it spoils the "falling" and emulsifying properties of the fluid and reduces the activity of the disinfectant by combining with the tar acids or phenols. In making a fluid the wisest plan is to let the works chemist calculate approximately the amount of caustic lye required for each pan charge and to employ a man to manufacture the fluid who possesses some knowledge of soap making.

There are numerous formulæ used for the manufacture of disinfectant fluids, each manufacturer using those which best fit in with his ideas or those of his customers. As a guide to the student, however, the following particulars may be useful.

Disinfectant fluid.

	Per cent.
Rosin	26
Light creosote, sp. gr. 1.025, approx. 18% tar acids	61
Petroleum, sp. gr. 0.815	3
Caustic soda	2.5
Water	7.5

With reference to the various high coefficient disinfectant fluids now on the market, these are generally made in works other than tar distilleries, and contain as their chief ingredients blast-furnace oil tar acids specially distilled and blast-furnace creosote.

Sometimes creosote is used in the manufacture of cheap lubricating greases for colliery trucks and bogies. The oil for this purpose must be of the heavy type, and the one most frequently used is that known as strained oil or " dead " oil. This oil has been referred to already in Chapter XV, page 187, and is obtained during the manufacture of crude anthracene. The specific gravity varies somewhat ; an oil testing 1.060 at 60° Fahr. is frequently used. These greases are prepared by adding rosin oil and slaked lime to the green oil. Usually the composition varies between 86 to 88 per cent. of heavy oil, 4 to 7 per cent. of rosin oil, and 4½ to 6½ per cent. of slaked lime, the remainder being water. In the brick industry creosote sometimes finds application under the name of brick oil. For this purpose it should possess a specific gravity between 1.060 and 1.070 and be quite free from " salts."

A suitable creosote for the manufacture of black varnish (usually a mixture of coal tar pitch, creosote and heavy naphtha, or of coal tar pitch, water gas pitch, creosote and heavy naphtha) must be free from an excess of naphthalene or anthracene salts, contain not more than 2 per cent. of water determined by distillation, and of a specific gravity between 1.050 and 1.065. A usual plan is to employ the higher gravity oils for slow drying black varnishes in which more flexibility in the film of dried varnish is desired, using perhaps a good proportion of water gas pitch in the composition. In the writer's experience, however, it has been found that all films made of the pitches and bitumens (whether heavy creosote or light creosote has been used) become very brittle in a short space of time, particularly those films made from a varnish in which water gas pitch has been used. This result is due not only to the original somewhat brittle nature of the pitch or bitumen, but also to the action of sunlight and diffused light, which seems to bring about changes in the nature of the material, probably by auto-oxidation.

As a wood preservative creosote oil is, without doubt, the finest material extant, and more of it is used for the preservation of railway sleepers and other timber in connection with railway work, and also timber used in telegraph installations, than in any other direction. It may be added here that the United States of America are the largest consumers of this material, using upwards of 108,000,000 gallons per annum. Large quantities are, of course, supplied to the British and Continental railway companies by manufacturers in this country, in addition to exporting very considerable quantities to the States. All this creosote is sold according to specification, each buyer having his own. This will of course necessitate in many cases careful mixing of several grades of oil, and even the removal of a certain amount of tar acids and sometimes the whole of the naphthalene. In other cases it is often necessary to add naphthalene before the creosote will answer the requirements of a certain specification. In order to give some idea of the various requirements of specifications, several are given in Table XXII, and three other specifications for creosote such as used on some American railroads are given in Table XXIII.

It is not convenient to discuss here whether a creosote containing a high percentage of naphthalene and tar acids or one containing a small quantity of tar acids and no naphthalene will give the best results as a wood preservative. According to many investigators excellent results have been obtained with both kinds, and at present the matter will have to be left at that so far as this book is concerned. Tests to prove the efficiency of a creosote for railway work take a number of years, and weather and soil conditions, etc., will influence the results in a variety of ways.

In the important process of stripping gas of its benzol, creosote has found a use, and it is probable that as time goes on the quantity required for this purpose will increase. The quality of the creosote destined for this purpose must receive careful consideration, especially in connection with the content of water and salts. Not more than traces of water should be allowed, and if the best results are desired there should be an entire freedom from naphthalene or anthracene salts. In regard to the specific gravity, this varies according to conditions laid down by different users, the variations being between 1.01 and

1.050. The distilling range varies for a similar reason. Some users prefer a creosote of a specific gravity between 1.01 and 1.02,

TABLE XXII

	Specific Gravity.	Water	Phenols	Naphthalene.	To be liquid at	Distillation.	Apparatus.
a	1.050-1.060 at 15.5° C	3 per cent.	10 per cent.	30 per cent at 15.5° C	38° C	Residue above 315° C 25 per cent.	Retort
b	1.040 at 27° C.	2 per cent.	8 per cent	Not stated	32° C	Below 315° C. Not more than 75 per cent	Wurtz flask
c	1.040-1.050 at 15.5° C	3 per cent	4-12 per cent	Not less than 20 per cent at 15.5° C	Not stated	Not stated	-
d	1.090 at 20° C	2 per cent	Not stated	Not stated	25° C	Below 315° C Not more than 60 per cent	Not stated
e	1.030 at 15.5° C	3 per cent.	Do.	Do.	32° C	Above 260° C 25 per cent.	Do.
f	Not stated	3 per cent	Do	Do	15.5° C	No distillate below 200° C Not more than 70 per cent. at 280° C	Do.
g	1.000-1.030 at 15.5° C.	2 per cent	18 per cent min.	Nil	0° C	Not less than 50 per cent at 265° C Not less than 80 per cent. at 315° C.	Do.

TABLE XXIII

Grade.	Sp. gr. at 38° C.	Liquid at	Distillation.				Water.
			At 200° C.	210° C.	235° C.	355° C.	
No. 1	At least 1.03	38° C.	None below	Not over 5% below	Not over 25% below	Above, if exceeding 5% must be soft.	Not over 3%
No. 2	Do.	38° C	Do.	Not over 8% below	Not over 35% below	Do.	3%
No. 3	Do.	38° C.	Do.	Not over 10% below	Not over 40% below	Do.	3%

which, when submitted to a distillation, in a retort yields 85 to 90 per cent. under 300° C. Others one of a specific gravity of about 1.035, and which will not begin to distil below 200° C. and yields 70 per cent. between this point and 280° C., when distilled in a retort. P. D. Walmsley and H. A. Morfey[1] give the following as a representative test of a suitable creosote for benzol recovery purposes.

Distillation portion of test carried out in a retort with the bulb of the thermometer immersed in the creosote.

Specific gravity	1.035
Dropping point	210° to 220° C.
50 per cent. distils over at	250° C.
80 ,, ,, ,,	300° C.
Water content	traces.

On cooling the distillate obtained up to 300° C. to 45° Fahr., and maintaining this temperature for thirty minutes, the solid naphthalene settling out, on being filtered and pressed, should not amount to more than 7 per cent.

Dr Colman's specification of a creosote oil suitable for the oil washing of gas is as follows :--

Specific gravity at 60° Fahr.	1.010 to 1.030.
Tar acids	Immaterial.
Naphthalene	Should deposit no naphthalene on being cooled down to 55° Fahr.
Boiling point	Should not boil below 200° C.
Distillation	Should distil not less than 70 per cent. up to 300° C. nor more than 90 per cent.

For storage of creosote second-hand boilers may be used. Very frequently large tanks built of iron plates or reinforced concrete, as described in Chapter II, are provided for this purpose, and it is policy to cover them. A closed steam coil, or coils, should always be placed in the tanks, the diameter of the tubing varying between 1 inch and 2 inches according to the size of the storage tank. At convenient points in the suction and delivery mains to and from the storage tanks a 1-inch steam inlet should be fitted. This will enable the pump man to clear the mains with open steam after pumping, a most necessary proceeding when "salty" creosote has been passed through the mains.

The fact that creosote is volatile and that this volatility does not depend upon the presence of naphthalene altogether, if at all, must be borne in mind when considering the question of storage. A few rough volatility tests carried out by the author will illustrate this point, see Table XXIV. Flat dishes 6 cm. in diameter were employed, giving a surface area of approximately 28.25 sq. cm., and the material was placed in the dishes to a depth of 0.5 cm. Some creosote oil was freed from tar acids by extraction with caustic soda and naphthalene by chilling to 0° C. and filtration, and the specific gravity of this treated oil was 1.035. A portion of this oil was used in the test in this state while to another portion was added tar acids and naphthalene, as indicated in Table XXIV, before submitting to the same conditions of test.

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[1] "Some notes on Benzol Recovery and Rectification." Read before Manchester District Institution of Gas Engineers, Oct. 28th, 1916. *Gas World*, Nov., p. 410.

TABLE XXIV

Hours' exposure.	Creosote free from tar acids and naphthalene		Creosote containing 10 per cent tar acids and 25 per cent naphthalene		Ground candle naphthalene	
	Loss at 60-65° Fahr.	Loss at 100° Fahr.	Loss at 60-65° Fahr.	Loss at 100° Fahr.	Loss at 60-65° Fahr.	Loss at 100° Fahr.
	Per cent.	Per cent	Per cent	Per cent	Per cent	Per cent.
24	1.38	3.42	1.10	3.30	..	1.00
48	2.42	6.10	..	..	0.90	2.20
96	4.61	10.40	4.10	11.60	2.31	3.32

With reference to the methods of testing, unfortunately at the present day there are no standards, and to a large extent each chemist uses his own method for the determination of one or more constants. Some of the tests in use are given in Chapter XVIII.

Table XXV which gives the degrees Twaddel, specific gravity and gallons per ton will, no doubt, be found useful for reference when dealing with creosote.

TABLE XXV

°Tw.	Sp. Gr.	Galls. per ton
12	1.060	211.32
11	1.055	212.32
10	1.050	213.33
9	1.045	214.35
8	1.040	215.38
7	1.035	216.42
6	1.030	217.46
5	1.025	218.53
4	1.020	219.60

CHAPTER XVIII

GAS STRIPPING

The "C" process—gas stripping by use of wash oil—plant required for gas stripping—washers—benzolised oil tank—heat exchangers—preheaters—still—condenser—separator—crude benzol receivers—oil coolers—debenzolised oil tank—pumps—meters—advantages secured by using oil for gas stripping—description of process—kinds of wash oils—effect of tar acids in wash oil—effect of water in wash oil—how to keep water out of wash oil—steam supply to still—theory of extraction of benzenoid hydrocarbons from gas—amount of wash oil in circulation—supply of wash oil to washers—reaction surface in washers—temperature of gas and wash oil—thickening of wash oil—debenzolising wash oil—cooling water—speed wash oil should travel through still—dephlegmation to separate naphthalene—grades of crude benzol—composition of crude benzol

SINCE 1914, owing to the increased demand for toluene required for the manufacture of explosives, many gas companies have adopted a system of washing their gas with tar. This system is known as the "C" process and it results in removing some of the benzene and toluene from the gas and, of course, increasing the percentage of these materials in the coal tar. The following figures will illustrate this: Normal tar from vertical retorts (intermittent system) yielded 0.75 gallon of toluol per ton, whilst a tar from the same system after being employed in the "C" process yielded 2.49 gallons of toluene per ton. Several workers have found that the addition of a small quantity of powdered limestone to the coal before carbonisation increases the yield of toluene in the tar, especially when used in connection with the "C" process. G. Stevenson[1] of the Long Eaton gasworks gives the following figures, Table XXVI, which illustrate

TABLE XXVI

	Normal Carbonisation "C" Washing.	Limestone used No. "C" Washing	Limestone used plus "C" Washing.
Crude naphthas	176 c.c.	320 c.c.'s	508 c.c.'s
Middle oils	720 c.c.'s	850 c.c.'s	800 c.c.'s
Toluene in tar, lbs per ton of coal	0.27	0.41	1.01

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[1] *Gas World*, Jan. 29, 1916, page 103.

this statement. In each case the coals used were low-grade Tupton "Derbyshire" seam, the temperatures used in carbonisation were the same, and the results were not obtained at the expense of either the quality or quantity of the gas. In each determination 9000 c.c.'s of tar were taken.

In the "C" process the temperature of both the gas and the tar have an important bearing on the amount of benzene hydrocarbons taken up by the latter; the higher the temperature the less the amount given up by the gas to the tar. The temperature of the gas at the gas inlet to the washer should be about 65° Fahr. and that of the tar inlet about 60° Fahr. This will mean that the tar must be cooled as well as the gas, and unless the cooled tar is thin like vertical retort tar, more or less unsuccessful working will result. The tar can be cooled by passing through a series of pipes which are water cooled by allowing cold water to trickle over them. Washers similar to those used for the removal of ammonia from gas are quite suitable for the carrying on of the "C" process.

The amount of tar made at the gasworks is not sufficient to remove the whole of the benzene hydrocarbons from the make of gas, and according to Geoffrey Weyman[1] the maximum efficiency of the "C" process is about 50 per cent., at which about 0.15 gallon of toluene and 0.9 gallon of benzene are left in the gas.

A far older and much more efficient and satisfactory process is that of gas stripping by the use of a suitable wash oil. It appears that Caro in 1869 was the first worker to use tar oils to remove benzenoid hydrocarbons from coal gas. Later, in 1882, George E. Davis and Josiah Hardman each patented a process for recovering benzol from gas by the use of tar oils, the former working his process in Manchester and the latter at Thorncliffe. Shortly after this coke oven works' owners began to consider the recovery of the by-products from their coke ovens, and much experimental work was done in connection with the recovery of benzol from the gas, based on the ideas of the pioneer workers just mentioned. This experimental work has resulted in the production of some very efficient processes, and at the present moment (1917) the estimated amount of benzol recovered from coke oven gas is approximately 38 million gallons per annum.

Recently, owing to the great European crisis, this process of stripping gas has been introduced into gasworks practice, and many gasworks, both large and small, are carrying it out with every success. It is highly probable, if the adoption becomes general, that a yearly production of about 55 million gallons will result. At the outset there were fears that the stripped gas would displease the consumer and would prove unsuitable for use in the flat-flame burner, but these fears have

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[1] "The Effect of the War on Gasworks Practice." Before North of England Gas Managers' Association. *Gas World*, May 13, 1916, p. 444.

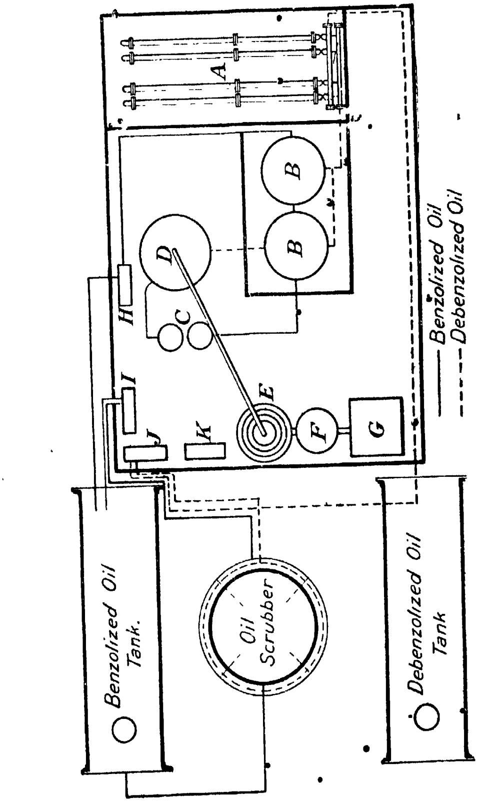


FIG. 68.—Diagrammatic Plan of General Arrangement of Gas Stripping and Crude Benzol Recovery Plant.

not been realised. Partly debenzolised gas has proved quite suitable as a heating medium and for lighting purposes, the gross B.Th.U.'s being reduced only about 4½ per cent., and with a modified flat-flame burner it gives quite satisfactory results. Needless to say, with a gas mantle the result is all that can be desired. Completely stripped gas can be enriched by the use of carburetted water gas, or by spraying it with paraffinoid hydrocarbons.

The plant required for stripping coal gas and debenzolising the wash oil need not be a complicated one. Briefly, it consists of a washer or scrubber, a benzolised oil tank, heat exchangers, preheaters, still, condenser, separator, receivers for crude benzol, oil coolers, a debenzolised oil tank and the necessary pumps. Reference to Figs. 68, 69, and 69A will give the reader an idea of the arrangement of this plant.

With reference to the kind of washer or scrubber, this may be of any efficient type as now employed in a gasworks for the purpose of ammonia recovery. The ordinary tower scrubber filled with boards, the Livesey washer, the Walker purifying apparatus with rocking arrangement, and several types of rotary scrubber have been used with success. In the case of the scrubber filled with boards it is as well to distribute the wash oil at the top of the apparatus by means of several Gurney's jets. Provision must be made, say by the use of T pieces and plugs, to allow the jets to be poked through with a wire should they become obstructed, and it is also necessary to supply the wash oil at a pressure sufficient to cause a forcible impinging on the discs of the jets. If this is not done the oil will not be sprayed in an efficient manner. Some works have found it an advantage to arrange that the upper half of the washer be supplied with debenzolised oil and the lower half with re-circulated partly benzolised oil. In other works two separate washers are employed, one for the debenzolised oil and the other for partly benzolised oil, providing for the unwashed gas to enter first that washer supplied with the partly benzolised oil. As the efficiency of the stripping process depends upon the reaction surface presented by the packing in the scrubber and the length of time the gas and wash oil are in contact, due consideration must be given to these matters and a scrubber put in of sufficient size to deal with the daily make of gas in a satisfactory manner. Dealing with a scrubber packed with the usual wooden boards, a surface area (reaction surface) of between 500 and 550 square feet should be allowed for each ton of coal carbonised per diem. These figures correspond approximately to 16 cubic feet and 18 cubic feet of tower space respectively. In order to properly control the supply and keep a constant head of wash oil, a feed tank of suitable size should be erected above the scrubber.

The benzolised and debenzolised oil tanks may be of any suitable shape and size. Cylindrical tanks made from second-hand steam boilers from which the tubes have been drawn and the ends blanked will serve this purpose admirably. A

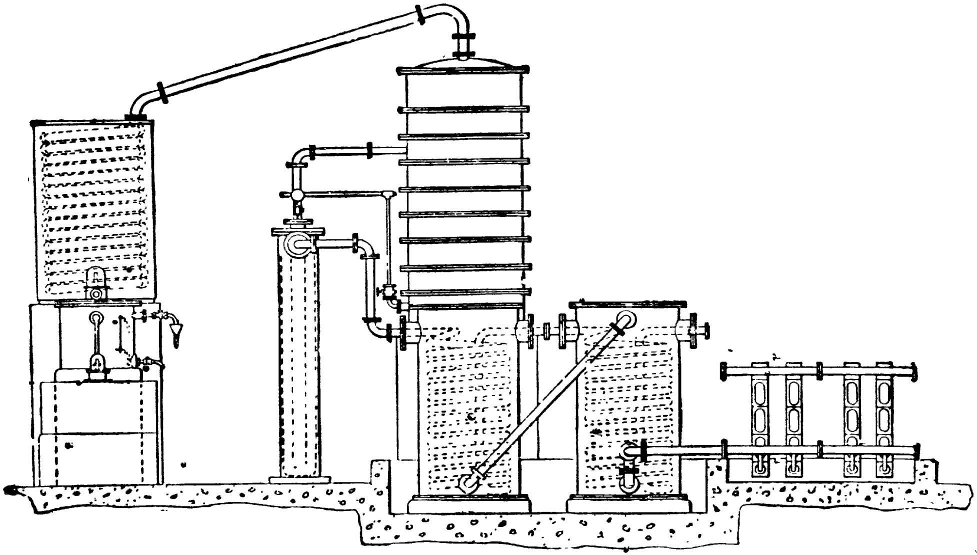
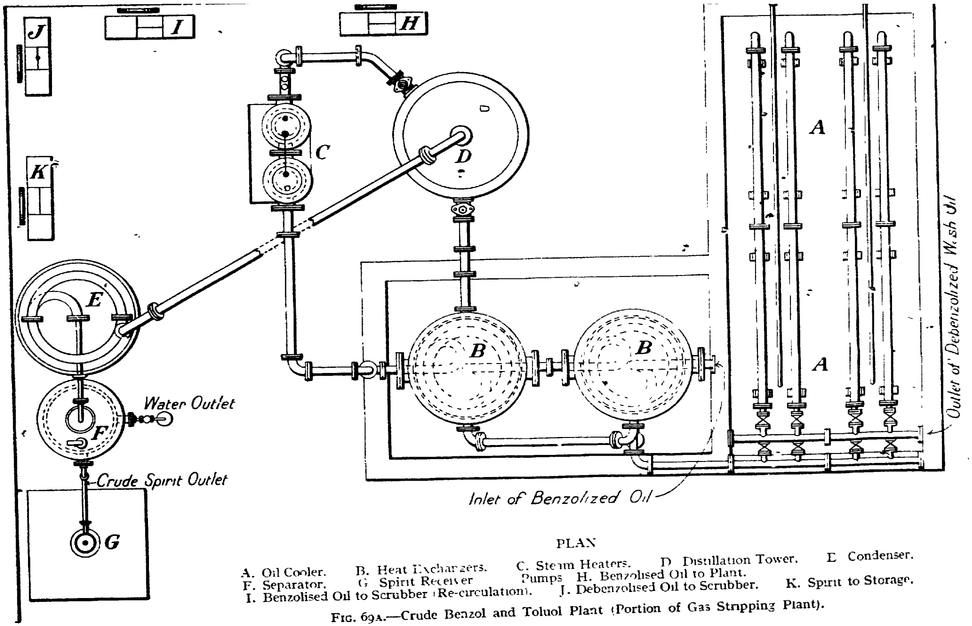


FIG. 69.—Elevation of Crude Benzol and Toluol Plant (Portion of Gas Stripping Plant).



PLAN

A. Oil Cooler. B. Heat Exchangers. C. Steam Heaters. D. Distillation Tower. E. Condenser.
F. Separator. G. Spirit Receiver. Pumps H. Benzolised Oil to Plant.
I. Benzolised Oil to Scrubber (Re-circulation). J. Debenzolised Oil to Scrubber. K. Spirit to Storage.

FIG. 69A.—Crude Benzol and Toluol Plant (Portion of Gas Stripping Plant).

manhole must be provided for the purpose of cleaning, etc., and also a hole for the inlet pipe at the top of the tank and another for the outlet pipe with its centre about 4 inches from the bottom.

Most benzol recovery plants have heat exchangers and steam heaters, through which the benzolised oil passes before it enters the still; others are provided with a preheater only, and there are cases in which these pieces of apparatus are dispensed with and the benzolised oil flows direct into a fire-heated still.

Heat exchangers are for the purpose of assisting in the cooling of the debenzolised oil after it leaves the still, and the heating of the benzolised oil in its progress towards that piece of apparatus. They consist of covered cylindrical or other suitably shaped tanks of cast- or wrought-iron, into which are placed coils of pipe constructed of either cast- or wrought-iron. Wrought-iron tanks and coils are suitable only in cases in which corrosion is slight, but when it is to be feared that ammonium salts such as the chloride are likely to be carried through the plant, then it is wise to use cast-iron, as this metal resists the corrosive action of ammonium chloride and other ammonium salts better than does wrought-iron. In order to facilitate the cleaning out of the tank, say after brushing down the coil, there should be provided a 1½-inch or 2-inch cock at the bottom; the slurry can then be flushed out through the cock. The hot debenzolised oil passes through the tanks and the benzolised oil through the coils, the former losing heat and the latter gaining it during this progress. The inlet for the debenzolised oil is placed at the top of the side of the tank and the outlet near the bottom. The coil inlet and outlet are at the top of the tank, and the coil is so arranged that after it enters the tank it falls in a straight piece to the bottom and then rises in the form of laps until it reaches the outlet. It is unwise to make the laps too close together; a distance of about 3½ inches between each lap must be allowed, and the outside of the coil should be not less than 6 inches from the inside of the tank.

In some plants the hot debenzolised oil circulates through the coils of the heat exchangers and the benzolised oil which is to be heated through the tanks, and in cases like this it is recommended[1] to fit a vapour pipe to the cover of the tank to conduct away any benzol vapours which may be formed to a condensing coil, and also to put in a baffle chamber to prevent any wash oil being carried over into the condensing coil.

The object of the preheater is to raise the benzolised oil to a temperature just before entering the still at which the maximum amount of crude benzol will be removed from the oil, and which will prevent the entanglement of water by the wash oil and enable the oil to leave the still carrying a minimum quantity of water. A preheater consists of a covered cylindrical, square or rectangular tank, containing a steam coil arranged in the form of laps. In cases in which corrosion is anticipated the tank and coil must be of cast iron for the reason just mentioned when dealing with heat exchangers, otherwise the tank may be of mild steel and the coil of wrought-iron steam pipe. Where corrosion has to be considered J. A. Wilson[1] recommends the following as a good construction for a preheater. A rectangular tank "built up of a few strongly flanged sections, with cast-iron U-pipes for the steam, these to be free at one end and jointed to the outside of the still at the other, the pipes being connected to each other by short U-bends, and being fixed horizontally, so that the oil will have an impinging action on them in its upward flow through the preheater." This worker advises against the use of gilled steam pipes, as they readily collect solid matter as it is deposited from the oil and thus reduce the heating efficiency of the coil. As a deposit of some sort is likely to form on any type of steam pipe it is advisable to arrange for a means (an easily removed cover, for instance) by which the coil can be brushed down from time to time, and in this connection it is a good plan to fit a 1½-inch or 2-inch cock to the bottom of the tank, through which the slurry can be removed. The laps of the coil should not be too close together; a distance of at least 4 inches being allowed between each lap. The inlet for the benzolised oil is on the side near the bottom of the preheater tank and the outlet on the opposite side near the top. It is advisable to fit a vapour pipe to the cover in order that any crude benzol vapours which come off from the heated benzolised oil may be conducted to a condenser coil. It can be so arranged that this vapour pipe leads to the condenser coil which is connected to the vapour pipe of the still.

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[1] *Gas World*, Nov. 18, 1916, p 460.

Where it is intended to adopt fire heating for the purpose of distillation a still of the pot type can be used, similar in construction to that illustrated on page 31, Fig. 12, but without the internal steam pipes. It is constructed of wrought-iron or mild steel plates, with a cast-iron swan-neck and vapour pipe. In setting the still there is no need to put in a curtain arch.

The best kind of still, and the one used in the larger number of plants, is of the continuous type, and it consists principally of a tower built up of cast-iron segments or chambers. The design of these segments varies a little according to the ideas of the makers, but broadly speaking there is a great similarity. Each segment, with the exception of the top and bottom ones, has a plate cast on it, and each plate is provided with one or

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[1] "Some points in the recovery of Benzol." J. A. Wilson, read before the Coke Oven Managers' Association, Midland Section. See *Gas World*, Coking Section, Dec. 2, 1916, pp. 11-14.

two overflow pipes, and several inlets over which are placed hoods or dispersers. The inlets and overflow pipes are so arranged that a seal of oil remains on each plate. As a matter of fact the illustration of the column on page 134 gives a typical idea of the arrangement. The segments, with the exception of the top and bottom ones, are approximately 1 foot deep and 3 feet 9 inches to 4 feet in diameter, flanged, and provided with perfectly faced joints. The top segment is simply a shallow dome with an outlet cast on the top, in the centre, to which is fixed the vapour pipe. With regard to the bottom segment, this is much larger than those which compose the greater part of the still and there is no plate cast on it. Approximately the size is 3 feet 9 inches deep. On this segment are cast an outlet for the debenzolised oil and an inlet for the live steam supply. In some cases there is a second inlet for the purpose of introducing a steam supply to a closed steam coil. This latter arrangement is considered by many workers, and also by the writer, to be an advantage. The live steam is introduced into the still by means of two jets or a small open steam coil provided with a few perforations. On the third segment from the top is cast an inlet to which is connected the benzolised oil supply. It should be mentioned here that some stills are provided with a baffle chamber (which is fitted to the top segment) and on the top of which is fixed a vapour pipe. In cases like this the inlet for the benzolised oil is cast on the top segment of the still proper. The number of segments provided with plates varies somewhat according to the make of the still, but a good average is twelve when the still is not provided with an "outside" dephlegmator. If it is desired to connect a dephlegmator to the still then the latter must not be too high, *i.e.* there must not be too many segments in its construction, or else dephlegmation will take place where it is not wanted, that is in the still. The number of segments in cases like this should be about eight.

The purpose of an "outside" dephlegmator attached to the still is to remove much of the naphthalene from the wash oil and also to prevent it getting into the crude benzol. This excellent idea was advocated strongly by the late Mr G. Stanley Cooper, a clever and much respected worker, especially in matters relating to the coke oven and by-products industry. The construction of the dephlegmator varies according to the ideas of the maker or the designer. One type is very similar to that illustrated and described on pages 135 and 136. The diameter is, however, rather greater, being about 3 feet, and the over all length less, varying between 4 and 5 feet, and the water tubes are not quite so close together. Another type of dephlegmator is built up of several cast-iron segments, each water jacketed and provided with a plate on which are inlets, hoods and overflow pipes. The number of segments containing plates varies, but it is usually between five and six. In the tube dephlegmator the vapours from the still enter at the side, near the top, and the uncondensed vapours leave at the side, near the bottom, but in the plate type the vapours enter the side of the bottom segment and the uncondensed portion leaves at the top from an outlet cast in the centre of a shallow dome which is bolted on to the top section. In both types the condensed liquid, oil containing a quantity of naphthalene, leaves at the bottom and is conducted away to cooling tanks in which the naphthalene separates out. It is not wise to place the dephlegmator too far away from the still; a distance of about 4 feet is quite enough.

Cooling tanks for the purpose of receiving and cooling the oil which leaves the dephlegmator, in order that its excess of naphthalene may separate out, should be constructed of mild steel plates and erected under cover, but away from any source of heat. They should be shallow, say about 2 feet deep, and of any suitable length and width to suit the volume of oil to be dealt with. If a means of refrigeration is already in existence and an extension can be conveniently made to these tanks, it will be an advantage, so far as speed and complete separation of naphthalene are concerned, to use it. Circulating cold water through pipes resting on the bottom of the tanks acts fairly well in the summer time.

The condenser attached to the still consists of a length of wrought-iron tubing or several lengths of cast-iron pipe arranged in the form of a number of laps and placed in a cylindrical, square or rectangular tank according to convenience. Condenser tanks and coils have already been dealt with on pages 50 and 51.

A description of a suitable separator or divider will be found on page 53.

As a receiver for the crude benzol a cylindrical, square or rectangular tank constructed of mild steel plates can be used, according to convenience. It must be a covered tank, the joints of which should be double riveted and well caulked. On the top of the tank is a manhole with a tight-fitting lid, a hole, say 1½ inches, for the inlet pipe and a ½-inch hole which acts as an air vent and which can also be used for dipping purposes. A 2-inch outlet pipe is fitted on the side of the tank with its centre about 3 inches from the bottom, and it is as well to fit a 1½-inch drain cock on the bottom of the receiver. This will be found useful for cleaning purposes.

Oil coolers vary somewhat in construction. In some plants they consist of a number of flanged cast-iron pipes, placed horizontally, and connected with U bends, and arranged in tiers of six or more, or on the flat in a tank. In the case of the former arrangement the bottom tier of pipes is suspended in a tank, generally constructed of concrete, and all the pipes are water cooled, the upper tiers by means of water sprays or water trickling over them and the bottom layer by the water in the tank, which must, of course, be kept on the move. In the latter arrangement the pipes are totally immersed in water, of which there must be a plentiful supply passing through the tank. With reference to the area of cooling surface, see page 221.

Sometimes the cooler is constructed in a similar manner to an ordinary still condenser and placed in an uright position, or else it consists of a number of tubes swelled into two tube plates and fitted into a cylindrical iron vessel, the whole arrangement being placed in a vertical or horizontal position.

Pumps may be of any reputable make, either of the ram or centrifugal type. So far as efficiency is concerned the latter type of pump is the better to use, and as they are designed for high lifts, from 25 feet to 50 feet or even more, there need be no fear on this score. A special type of rotary pump suitable for dealing with wash oil is now on the market. It is capable of pumping oil at a temperature of 120° C. and can be used with a suction lift of up to 8 feet. This pump is made by the Roots Company of Connellsville and according to the makers 75 to 85 per cent. of the power applied to the operating shaft is absorbed in doing useful work.

It is a wise plan to provide a means by which the supply of debenzolised wash oil to the scrubber and also the supply of benzolised oil to the still can be controlled. This can be done by the use of a meter and a cock provided with a quadrant, feeding by gravity from a tank in either case. A gauze sieve must be placed before the inlet to the meter for the purpose of keeping back particles of solid matter, and the sieve should receive regular inspection to see that this material is removed from it. With reference to the meter, a certain amount of trouble may arise in regard to corrosion, but there is no doubt that with proper representation makers will be induced to construct meters of a specially resistant metal.

The plant used in working up crude benzol, and that employed in making rectified benzol and toluol, has already been described in Chap. IX, and the reader is referred to it for information on this subject.

There are several advantages secured by using oil instead of tar to recover the lower benzenoid hydrocarbons from coal gas. The chief of these are:—

1. Variation in atmospheric temperature does not seriously affect the efficiency of the process; during the winter months the oil does not thicken up like tar.

2. The stripping of the gas can be carried out to completion or partially, as desired.

3. If the process is properly worked naphthalene is removed from the gas in a very efficient manner."

The benzol recovery process is a continuous one, the wash oil first passing through the scrubbers and from these to the benzolised oil tank, thence onward through the heat exchangers and superheater to the still. In the still the benzolised oil is relieved of its crude benzol, and then it passes through the heat exchangers and from these to the air coolers and finally to the debenzolised oil tank. From this receptacle it is pumped to the first scrubber and from this piece of apparatus the whole process is repeated. The wash oil continues in circulation until it becomes "spent" oil, which is thicker and its specific gravity and distilling range higher than that of the original "fresh" oil. It is then replaced by a fresh supply, or else a certain percentage of the wash oil is removed from circulation at regular intervals.

The quality of the wash oil plays an important part in the efficiency of working and should receive due consideration. Several kinds of oil have been suggested as suitable for use in the stripping of gas, the chief of which are:—

Moderately light creosote oil.
Heavy creosote oil.
Strained anthracene oil (green oil).
Petroleum distillate (gas oil).
Shale oil distillate.
Blast-furnace oil.

Although the shale oil distillate and petroleum distillate (gas oil) possess good benzene and toluene absorbing powers they have not received general acceptance, chiefly on account of the risk there is of obtaining a crude benzol containing paraffinoid bodies. A crude benzol containing these bodies is not so valuable on the market on account of the difficulty, and in some cases almost impossibility, in separating the paraffinoid hydrocarbons from the rectified products. The fact that gas oil is free from naphthalene and is an excellent solvent for this substance is certainly in its favour. At the time of writing it is being used at some works with good results, but it is undoubtedly a well chosen oil. If a petroleum distillate which on distillation yields nothing below say 170° C. is employed the risk of obtaining rectified products containing paraffinoid bodies is much reduced, and with careful working up of the crude benzol satisfactory results may be obtained. When, however, oils of a different class (*e.g.* creosote oils) which introduce no risks of this kind can be easily secured, then it is wise to use them and to avoid paraffin oils.

In regard to the creosotes and strained anthracene oil, these materials seem to be in greatest favour and are used very largely, particularly the heavy creosote. It appears that a coal tar creosote boiling between 220° and 265° C. extracts benzol and toluol from coal gas better than the heavier coal tar distillates, but this is not the only factor in the case. Consideration must be given to the amount of wash oil (creosote) which will come over with the crude benzol during the debenzolising process. Using a creosote with a low distilling range will result in a larger amount of its lower boiling point compounds distilling over with the crude benzol than if a creosote of a higher distilling range be employed. In this respect it is an advantage to use one possessing a distilling range, say, between 250° and 325° C., although the benzol-toluol absorbing power is not quite so great. However, a creosote of this distilling range has one disadvantage, and that is its rather high viscosity when compared with lighter fractions. This results in rather a lower efficiency in regard to its stripping powers, especially during the cold weather, and it also renders the oil a little more difficult to cool after leaving the still. Bearing all these facts in mind, and with a desire to secure as high an efficiency as possible, it is best to use a creosote with a medium distilling range and to employ careful dephlegmation to separate from the crude benzol, immediately it leaves the still, as much as possible of the wash oil which is carried over. One of the best specifications of a creosote for gas stripping which has come to the writer's notice is that given by Walmsley and Morley. This has been referred to in Chap. XVII, page 199, but for the sake of convenience the distilling range is given here. It is :—

Dropping point	210°–220° C.
50 per cent. distils over at	250° C.
80 ,, ,, ,,	300° C.

Although the distilling range of strained oil (green oil) is high it is not so suitable as heavy creosote on account of its high viscosity and its low benzol-toluol absorbing property. A strained oil having a specific gravity of 1.100, on distillation in a Wurtz flash, the thermometer being in the vapour, bulb opposite the outlet, showed —

up to 220° C.	9 per cent.
,, 240° C.	14 ,,
,, 260° C.	18 ,,
,, 280° C.	28 ,,
,, 300° C.	40 ,,

Further specifications of creosotes used in the process of gas stripping are as follows :—

(*a*)[1] Specific gravity at 60° Fahr.	1.040
Tar acids	8 per cent.
Distilling up to 200° C.	0 ,,
,, ,, 220° C.	20 ,,
,, ,, 240° C.	35 ,,
,, ,, 260° C.	65 ,,
,, ,, 280° C.	75 ,,
,, ,, 300° C.	85 ,,
(*b*)[2] Specific gravity	1.037
Naphthalene	21.6 per cent.
Below 200° C.	0.5 ,,
,, 220° C.	16.5 ,,
,, 240° C.	40.5 ,,
,, 260° C.	61.0 ,,
,, 280° C.	70.0 ,,
,, 300° C.	78.0 ,,

It will be observed that in the last specification the content of naphthalene is high, particularly for a wash oil. The naphthalene trouble is the gasworks managers' "nightmare," and any means by which this trouble can be reduced is always welcome. In the process of stripping gas the content of naphthalene in the gas is usually reduced by the solvent action of the wash oil, but if a wash oil is employed which contains an excess of naphthalene the opposite result will, in all probability, be obtained, particularly if the percentage of naphthalene in the gas, before washing, is low. It is desirable on this account to begin with a fresh wash oil practically free from naphthalene and to see to it that that which is picked up from the gas is removed during the debenzolising process by dephlegmation, or else allowed to crystallise out of the debenzolised oil by chilling and settling in suitable tanks.

That washing the gas with oil removes much of the naphthalene should be a strong recommendation to gas engineers to install a stripping plant, but in doing so they must not lose sight of the fact that the wash oil removes from the gas much of the material (benzene, toluene and xylene) which holds naphthalene in suspension, and that any naphthalene which still remains in the gas may deposit somewhere and cause trouble. This may be prevented by spraying into the gas (after it has been stripped) a suitable solvent by one of the well-known processes, and by doing this the gas will also be enriched.

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[1] *The Gas Chemists' Summary*, 1915, p. 82.

[2] "Effect of the War on Gasworks Practice." J. Weyman, M.Sc. See *Gas World*, May 13, 1916, p. 445.

At the present time (1917) blast-furnace creosote is receiving attention in connection with its suitability as a gas stripping material. It possesses the following advantages:

1. The naphthalene content is practically nil.
2. It is a good solvent for benzenoid hydrocarbons.
3. It is an excellent solvent for naphthalene, much better than coal tar creosotes.
4. It has a high distilling range. There is one disadvantage, and that is during the cold weather it is liable to become more viscid than a suitable coal tar creosote, with the results mentioned on page 213.

Unfortunately, the volume produced annually is much less than that of coal tar creosote, and this limits its use. It can, however, be mixed with the coal tar product with advantage. Owing to the high germicidal value of the tar acids contained in blast-furnace creosote it is much sought after by disinfectant manufacturers, who extract all or most of the tar acids, and who are generally in a position to supply the extracted oil in a condition eminently suitable for gas stripping. A specification of a blast-furnace oil is given by Geoffrey Weyman,[1] which is as follows:

Specific gravity	0.957
Naphthalene	trace
Below 220° C.	4 per cent.
„ 220° C.	7 „
„ 240° C.	24 „
„ 260° C.	40 „
„ 280° C.	58 „
„ 300° C.	72 „

Some particulars of blast-furnace oils which are at present being used for gas stripping are given in Table XXVII.

TABLE XXVII

Sp. Gr. at 15° C.	Tar Acids per cent.	Water per cent.	Per cent. up to							
			220° C.	240° C.	260° C.	280° C.	300° C.	340° C.	360° C.
0.961	5.0	0.5	3	7	20	43	55	80	89
0.960	4.6	trace	3	8	23	42	56	79	86
0.961	4.0	0.5	2	6	21	44	62	81	89

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[1] "Effect of the War on Gasworks Practice." See *Gas World*, May 13, 1916, p. 445.

The point as to whether it is an advantage to use a wash oil containing tar acids or not remains as yet unsettled. It is an established fact that tar acids are excellent solvents for naphthalene, while coal-tar hydrocarbons are very poor in this respect. This fact alone seems to decide in favour of using wash oils of the coal-tar creosote type which contain tar acids. These remarks do not apply to blast-furnace oil (tar acid free) as the hydrocarbons contained in it are excellent naphthalene solvents. To illustrate these facts the writer gives the following figures, Table XXVIII, obtained by him some time ago under strictly comparable conditions. In the table the solvent power of tar acids extracted from coal tar creosote is taken as 100.

TABLE XXVIII

Material.	Naphthalene solvent power
Coal tar acids from creosote . . .	100.0
Creosote oil containing 25 per cent. tar acid	26.5
Creosote oil free from tar acids . .	10.2
Blast-furnace oil free from tar acids .	108.9

The effect of water in the wash oil on its extractive power is one which requires careful consideration. Practice has shown that as the percentage of water in a wash oil rises, so does its absorptive (or extractive) power decrease. For instance, an oil containing about 3 per cent. of water will absorb approximately 36 per cent. less benzenoid hydrocarbons than a water free oil, while one containing 7 per cent. will absorb 45 per cent. less. When purchasing an oil for gas stripping it should be laid down that it must not show more than 0.5 per cent. of water when submitted to a distillation test. It must not be forgotten that there are other channels by which water may get into the wash oil. For instance, the gas carries a certain amount of water in the form of vapour, which, if the wash oil is at a lower temperature than the gas, will be taken up by it. It is necessary on this account to see that the wash oil as it enters the washer is at a slightly higher temperature than the gas, say about 2° C. Water may also get into the oil during its treatment in the debenzolising still if this piece of apparatus is steam heated. As already mentioned, steam heated stills are fitted with "live" as well as closed steam coils, and if the steam is wet, that which leaves the open steam coil will deposit water in the oil, particularly if the oil, as it enters the still, is at too low a temperature. To avoid this it is wise to superheat the steam a little or pass it through a water separator before allowing it to enter the still. If the benzolised oil is too low in temperature when it enters the still it may bring about condensation of the "live" steam even when this is supplied in a comparatively dry state. To steer clear of this the temperature at which the benzolised oil enters the still and that at which the debenzolised oil leaves it must be properly controlled. The temperature at both these points should be at least 10° C. above the boiling point of water, being a few degrees lower at the outlet than at the inlet. Various temperatures have been recommended from time to time, but in the opinion of the writer an inlet temperature of 115° C. and an outlet temperature of 110° C. will, in most cases, give satisfactory results. It must be borne in mind that the higher the temperature used in the still, the greater the possibility of forming decomposition products in the oil, and thus hastening its "thickening" and the shortening of time of service of all or part of it. Thickening of the oil is also brought about by the loss of the lighter portions during steam distillation in the debenzolising still, and in some cases by the tar which it picks up from the gas, when the gas is not quite tar free.

It is convenient at this point to mention again that the steam supplied to the still should be dry, and, with advantage, slightly superheated. That which passes through the closed coil, which is fitted in some of the debenzolising stills, will give good results if it is at a pressure of between 60 lbs. and 80 lbs. to the square inch. With regard to the "live" steam which enters the still *via* the perforated coil or steam jets, this must not be introduced at too high a pressure or some of the unfractionated oil will be blown over with the crude benzol. On the other hand, steam supplied at too low a pressure will not properly fractionate the oil, because as it meets the descending oil at each plate its temperature and pressure fall until finally it reaches a stage, near the top plates, at which it cannot sufficiently agitate and heat the oil nor "lift" the crude benzol vapours to the vapour pipe. Further, steam at very low pressures, unless superheated near the still, is very liable to be wet, and this, in addition to a fall of pressure due to the expansion in the still, will introduce the risk of some water being deposited in the oil. Steam is always reduced in pressure by throttling or wire drawing, and this process takes place when the steam passes the control valve and also when it leaves the perforations in the coil or jets. Hence a supply from a boiler at a very low pressure would be reduced further on entering the still, and in spite of the fact now to be mentioned it is not an advantage in this case. When steam is throttled or wire drawn it is rendered less wet than it was originally, and in fact if it is not inordinately wet it is dried and possibly superheated (this is not the case if the pressure is reduced by expansion). It follows from what has been said that steam should be supplied from a boiler working at a good pressure, say between 60 lbs. and 80 lbs. to the square inch; it must be dry; and it should enter the still immediately after being reduced in pressure by throttling with the control valve near the steam inlet. This valve can be carefully opened by the plant man and the supply of steam into the still regulated according to the flow of condensate from the worm end.

The benzenoid hydrocarbons exist in coal gas in the form of vapours, or for all practical purposes in the form of gases; liquids when converted into vapours obey all the laws of gases. In the process under consideration we may consider these bodies as indifferent gases when compared with the solvents used to extract them. The removal of active gases, *i.e.* those which will react easily with an absorbing medium, is a simple matter compared with that of the absorption of indifferent gases. In the former case chemical absorption can be brought about by the employment of a suitable absorbing medium and making use of the ionic state, but in the latter case, having non-electrolytes to deal with both in regard to the gases and the absorbing medium, it is not possible to take advantage of an ionic state, and the process will proceed much more slowly. Bearing in mind the law which governs the solution of gases in liquids, viz., "given a state of equilibrium, the concentration of a gas bears a constant relation to that of the solution," the term concentration indicating the amount present in a unit volume, we shall be able, briefly, to consider the theoretical side of gas stripping. Now, the concentration of a gas and the quantity of it which can be dissolved in a liquid are proportional to the pressure and, naturally, to the nature of the substance used as a solvent. Also, the temperature of both the solvent and the gas will exert their influence.

In the process under consideration the separation by absorption of gases (vapours) of a similar nature, *i.e.* the lower benzenoid hydrocarbons, from a mixture of dissimilar gases is aimed at, and the following points should be borne in mind. The unabsorbed gases (vapours) will carry away with them a certain amount of the material used as the solvent, this amount varying according to the vapour pressures. In any case it is not very considerable. It is necessary to use the *counter current* system of washing; to expose the largest possible reaction surface in regard to the gas and the solvent, together with sufficient time of contact; and to maintain a certain amount of agitation of the absorbing liquid (the wash oil). The reasons are as follows: As the absorption of the vapours of the benzenoid hydrocarbons goes on their partial pressure in the gaseous mixture becomes less, and it is therefore necessary, in order to obtain the greatest possible absorption to bring the strongest solution (partly benzolised oil) into contact with fresh or unwashed gas, and fresh wash oil into contact with partially washed gas. This can only be done by using the *counter current* system. The larger the reaction surface in the washer combined with a properly regulated supply of wash oil the greater will be the surface of contact between the gas and the solvent, the latter being spread out in thin films and the former well broken up into separate currents. Now the greater the surface of contact, combined with a reasonable limit of time for action, the more efficient will be the absorption of the hydrocarbons by the wash oil, this efficiency being increased, of course, by the adoption of the counter current principle as just mentioned. If the wash oil is agitated it is broken up into drops, and the smaller these drops the greater the surface of contact. Agitation is also necessary in order to assist in the dissemination of the dissolved gases throughout the wash oil. Agitation is obtained mechanically, *e.g.* by the use of the Walker purifying apparatus, or by force of gravity, *e.g.* in falling from one board to another as in the board-packed washers.

The amount of wash oil in circulation has an important bearing on the efficiency of the plant, and it should be carefully controlled after a decision has been come to as to the best volume to use. On plants in various parts of the country, the amount of wash oil used varies between 55 and 120 gallons per ton of coal carbonised. The volume should differ according to the degree of saturation aimed at, and this in its turn depends upon the efficiency of the washer and the time of contact between the gas and the wash oil. A good average is between 65 and 70 gallons of wash oil per ton of coal carbonised, and the degree of saturation about 4.5 per cent. If it is assumed that each ton of coal carbonised yields 3 gallons of benzenoid hydrocarbons and a degree of saturation of 4.5 per cent. is aimed at, then 67 gallons of wash oil per ton of coal carbonised will be required. On the same assumption, for a 4 per cent. saturation 75 gallons of wash oil will be required, and for a 3 per cent. saturation 100 gallons of wash oil. In the case of small works, where necessity requires that the benzolised oil be sold or returned to a larger works, then a degree of saturation as high as 9 per cent. is often aimed at. It is interesting to note that experience has shown that below a certain point the smaller the volume of wash oil used per ton of coal carbonised the greater is the amount of toluene and its higher homologues and the less the amount of benzene removed from the gas.

The supply of wash oil to the washer should be regular and at a constant head. If these conditions are varied from the correct standard found for the plant then there is a risk of the gas not being properly stripped or of the wash oil not being kept up to the required degree of saturation. A diminished head or supply may result in the boards, or other material providing the reaction surface, not being properly covered, and an increased head or supply will result in thicker films of wash oil and, therefore, a reduced contact surface.

Reference to the amount of reaction surface required in gas stripping is made on page 204. Satisfactory results will not be obtained if the figures there given are reduced to any great extent—in fact, it would in many cases be advantageous to increase them somewhat, say, for instance, to 20 cubic feet of tower space per ton of coal carbonised per day, representing approximately 120 square feet of reaction surface, if boards are used. These and the figures already given (page 204) are only approximate, and when a new plant is to be erected the type of washer to be adopted and also the extent to which the gas is to be stripped must be considered.

One of the most important factors governing the successful recovery of the benzene hydrocarbons from gas is that of temperature. The temperature of both the wash oil and the gas to be stripped must be carefully controlled. If the temperature of the wash oil is too low when compared with that of the gas, then there is a risk of naphthalene being taken up from the former (in cases in which the percentage is fairly high) by the latter, and on the other hand, if the wash oil is at too high a temperature compared with that of the gas, then less benzenoid hydrocarbons will be extracted. It is necessary, however, for the wash oil to be at a slightly higher temperature than the gas in order to prevent water being deposited in the oil; this difference should be about 2° C. Good results can be obtained by keeping the gas at about 18° C. and the wash oil at about 20° C. E. W. Smith[1] recommends that the temperature of the wash oil should not be higher than 22° C. in order to secure the best working results.

It may be as well to mention in this place that it is advisable to remove the ammonia from the gas before passing it along to the stripping plant. If this is not done then there is, naturally, some loss of ammonia due to the deposition of ammonium salts in parts of the plant, also there is the risk of increasing the corrosion of some of the units of the plant by certain of the ammonium salts, for instance ammonium chloride, and the reducing of the absorbing power of the wash oil.

During each cycle the volume of the wash oil is reduced by a small amount. This is mainly due to the fact that some of the lower boiling constituents of the oil are carried over with the crude spirit during the debenzolising process. This amount should be replaced each day by fresh wash oil. It is also necessary to do this to reduce to a certain extent the "thickening" of the oil. Eventually, however, the oil becomes "thick" (i.e. the specific gravity, viscosity, and drop point of the oil become higher), and its power of absorbing benzenoid hydrocarbons is reduced. On this account it is put out of commission and a new lot of wash oil supplied to the plant. The "thickening" of the wash oil can be stayed for a considerable period if a certain proportion is removed each week and replaced by fresh wash oil. In this connection E. W. Smith[1] recommends the removal of 10 per cent. of wash oil from circulation per week when using 50 to 70 gallons per ton of coal carbonised. It is advantageous occasionally to add fresh wash oil somewhat lighter in specific gravity to the original, but before doing this the debenzolised wash oil in circulation should be examined in the chemical laboratory for its physical constants.

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[1] See *Gas World*, Dec. 16, 1916, p. 541.

Care must be taken that the debenzolising of the wash oil is properly carried out before returning it to the washers. A partly debenzolised oil will not absorb the desired amount of benzenoid hydrocarbons, and on this account the efficiency of the stripping plant will be reduced. The oil as it leaves the still should be examined periodically in the chemical laboratory.

Another factor upon which the efficiency of a stripping plant depends is an adequate supply of cooling water for the condenser attached to the debenzolising still (also for the condenser of the rectifying still if this is attached to the plant), and also for the water condenser through which the debenzolised oil passes before entering the storage tanks or receivers. In the case of the debenzolising still condenser a flow of about 2½ gallons of cooling water for each 1 gallon of distillate condensed is a suitable figure to work upon, and for a rectifying still condenser 5 gallons for each 1 gallon of distillate. For the debenzolised oil coolers an allowance of say 1½ gallons of water per square foot of condensing surface per hour will prove suitable under most circumstances. A useful and usually safe allowance to make in calculations connected with condensing surfaces for this purpose is 1000 B.Th.U.'s per square foot per hour, these units being carried away by the cooling water.

When distilling the benzolised oil (i.e. removing the benzenoid hydrocarbons) care must be taken to see that the temperature of the benzolised oil at the inlet and that of the debenzolised oil at the outlet are properly controlled. The correct temperatures to use and the reasons for their employment have already been given on pages 216 and 217. If the number of compartments or segments in the still is insufficient, then the oil under treatment will leave the still too soon and consequently will not be properly debenzolised. This bad result will also occur if the design of the plates of the segments is faulty or if the oil is passed at varying speeds through the still. A constant speed must be arranged for. If the oil is supplied to the still in too great a volume, then a choking of the compartments will take place (even when properly designed overflows are provided), and there is a likelihood of benzolised wash oil being carried over with the steam and crude spirit vapours. The most suitable speed at which the oil should travel through the still of any individual plant can be found by examining the wash oil, as it leaves the still, for its content of benzenoid hydrocarbons. When this speed is found laboratory control must not be discontinued, but a daily test carried out on a bulk sample made up of samples collected by the plant man say every two or three hours. The debenzolised oil as it leaves the still when submitted to a distillation test in the chemical laboratory should not yield more than say 0.3 per cent. up to 160° C.

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[1] See *Gas World*, Dec. 16, 1916, p. 541.

On page 209 mention was made of the use of a dephlegmator for the purpose of facilitating the removal of much of the naphthalene contained in the debenzolised oil, some of which was possibly in the fresh wash oil and much of which has been taken up from the gas. The temperature at which the vapours leave the outlet of the dephlegmator must be taken from time to time and kept under control, and although a certain amount of latitude can be allowed, any variation must be made with an object in view and not carelessly. For instance, the temperature must be varied according to the "strength" at which it is desired to produce the crude benzol, or the percentage of saturation of the benzolised oil. Temperatures between 90° and 95° C. are used with good results, but it is wise for the manager to adjust his own temperature according to conditions obtaining in his particular case. If the dephlegmator is used properly the naphthalene trouble will be considerably reduced, if not wholly done away with.

Various grades of crude benzol are made on recovery plants, and some of these are 65 per cent., 60 per cent. and 55 per cent., these percentages representing the amount of distillate which comes over up to 120° C. when 100 c.c.'s are distilled in a glass retort with the thermometer immersed in the liquid.

The composition of the crude benzol will vary a good deal according to the "strength" or the percentage it gives up to 120° C. on distillation; the quality of the wash oil used; the degree of saturation of the wash oil, and so on; in fact, it is questionable whether two lots will be found alike. In a recent paper[1] Weyman gives the following figures: benzol, about 55 per cent.; toluol, 9 per cent.; solvent naphtha, 10 per cent.; bottoms, 26 per cent.

With regard to the distillation of the crude benzol, and the rectification of the products, methods and plant for doing this are described in Chapters IX, X, and XI. Since writing this chapter an excellent paper, one might almost say a classical paper, on "Some Physico-Chemical Considerations on Benzol Recovery from Coal Gas," has been published by Mr T. F. E. Rhead, M.Sc.,[1] and the writer recommends all those interested in the important subject of benzol recovery to give this paper their careful study.

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[1] "The Effect of the War on Gasworks Practice," Geoffrey Weyman, M.Sc. See *Gas World*, May 13, 1916, p. 444.

In the *Journal of the Society of Chemical Industry* of February 15, 1917, there occurs a paper by Dr. R. Lessing entitled, "Extracting the Vaporous Constituents from Coal Gas." This communication deals with a suggested method of debenzolising gas by "dry" scrubbing and a method of determining the amount of benzenoid hydrocarbons in coal gas, and it should receive the serious consideration of all who are interested in gas stripping.

The diagram Fig. 70 illustrates the Southport debenzolising plant, which has been erected from material found on the Southport gas estate. Similar material is usually found on most gasworks or can be readily procured at small cost. The whole of the plant was erected in ten days' time at a cost of £25 (labour only), and it has been working for some considerable time, during which it has given entire satisfaction. The diagram shows the simplicity of the apparatus, and apart from the small amount of labour required on the furnace very little supervision is necessary.

The benzolised oil is continuously pumped into an overhead syphon which is fitted with an overflow. By the regulation of a cock marked A on the plan a regular supply of oil is maintained. The benzolised oil passes through a heat exchanger H and enters at the bottom of the twin heating tubes at points B. Connected to the inlet pipe there is an extension pipe to the debenzolised oil cooler, which pipe is fitted with a cock so that at any time the oil can be drained out of the heating tubes, the end flanges removed, and the tubes cleaned when necessary. The oil passes out of the 16-inch heating tubes by means of two 2-inch pipes, at the top of which are mounted thermometers. These thermometers are fixed into the top plugs and made tight by cement. The tubes are connected to the chamber C in the middle of the fractionating column. The benzolised oil, which is heated to a temperature of between 110° and 120° C., passes into the lower portion of the fractionating column through a quantity of steel turnings and rings, as shown in the diagram. At the base of the column there is a small chamber into which a volume of steam is passed. The steam meets the hot oil as it passes through the mass of turnings and rings. It should be noted that the upper portion of the column is filled in a similar manner to the lower portion. By a proper adjustment of the steam, a 65 per cent. benzol can readily be obtained from the benzolised oil. It is possible to obtain as high as 80 per cent. benzol, but if this quality is maintained a certain amount of benzol returns with the oil to the storage tank.

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[1] See *Gas World*, Jan. 27, 1917, pp. 61-66.

The benzol condenser D is made from 2-inch lead pipe, and is attached to a small syphon pot at the lower end in which a separation of the water from the benzol is effected.

In the working of the Southport plant the steam is so regulated that the condensed water coming along with the benzol is equal in volume to the crude benzol.

The plant is capable of debenzolising 250 gallons of benzolised oil per hour, and the maximum amount, 264 gallons of 65 per cent. benzol, may be recovered in one day.

CHAPTER XIX

TARWORKS' TESTS

Examination of tar—pyridine tests—pitch tests—examination of creosote oil—benzol testing—valuation of crude naphtha—naphtha testing—valuation of light oil—cresylic acid tests—testing metacresol by the long or short cresylite test—carbolic acid tests—anthracene tests—examination of caustic liquors, spent liquors and lime mud—testing coke furnace gases—examination of coke—determination of benzenoid hydrocarbons in coal gas—testing benzolised and debenzolised oil—determination of naphthalene in coal gas—Dr Colman's method of estimating the percentage of benzene, toluene, and xylene in toluol.

EXAMINATION OF TAR

Water.—A quick method of determining this substance in tar is as follows: One hundred grammes of tar are weighed into an 8-oz. tubulated retort with a long beak, and 20 to 28 c.c.'s of benzol added. The lot is mixed together carefully, and the retort is then suspended on a retort stand. A small flame, preferably that obtained with a Rose burner, is placed under it, and the water and benzol which comes over collected in a measure placed under the beak of the retort. The speed of the distillation must be regulated so that the whole of the distillate is condensed. With this method, the water comes over between from ¾ of an hour to an hour, without frothing.

Another method which gives excellent and rapid results, but which requires a little more apparatus, is carried out as follows: Into the tubulure of an 8-oz. retort is fitted a funnel sufficiently large to hold 150 grammes of tar. The stem of the funnel is shortened and the bore closed by heating in a flame to produce an orifice of about 3/32 inch in diameter. On the end of a length of glass rod a small piece of india-rubber tubing is placed, and this is inserted into the stem of the funnel, as shown in Fig. 71. A 100 c.c. measure is required to collect the distillate. The retort must have a long beak, or, better, should be connected to a 12-inch Liebig condenser. Into the retort is placed about 50 c.c.'s of heavy naphtha, free from naphthalene, and 100 grammes of tar are weighed into the funnel. The naphtha is now brought to a boil, and immediately the same commences to distil the tar is allowed to run into it through the small orifice in the funnel stem. It will be found that in a few minutes after the tar has left the funnel the whole of the water contained therein has distilled over. With care this operation requires from between 20 minutes to half an hour. S. R. Church recommends the following method: Measure 50 c.c.'s of coal tar naphtha, or light oil (which must be free from water), in a 250 c.c. measuring cylinder. Two hundred c.c.'s of tar are then added and the lot mixed. Transfer the contents of the cylinder to a small copper still, and wash out the cylinder with 50 to 75 c.c.'s more of naphtha, adding the washings to the contents of the still. The still is connected up to a tube condenser having a water jacket 15¼ inches long. Heat is then applied by means of a ring burner and distillation carried on until the thermometer indicates a temperature of 205° C. The distillate is collected in a separatory funnel, into which 15 to 20 c.c.'s of benzol have been previously placed. The addition of the benzol effects a clean separation of the water from the oil. The water is run off into a measure and the volume read.

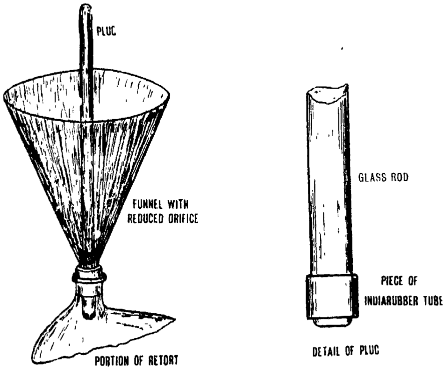

FIG. 71.—Funnel and Plug used in determining Water in Tar.

Specific Gravity.—Frequently the specific gravity of tar is taken by means of a Twaddell hydrometer. In carrying out the test with this instrument, the tar should be brought to 60° Fahr. (15.5° C.). When this temperature is obtained, the hydrometer is carefully placed in the centre of the tar, which is contained in a specific gravity jar, and plenty of time allowed for the hydrometer to sink.

Church recommends the following method for taking the specific gravity of tar: Between 300 to 400 c.c.'s of tar are dried in the same apparatus as used for the water determination but without the addition of naphtha. The distillation is carried on until a temperature of 170° C. is reached. Any oil which has distilled over is carefully separated from the water and returned to the tar in the still and thoroughly mixed in after cooling. The specific gravity is carried out on this dehydrated tar in a specific gravity bottle of the Hubbard type, whose water capacity at 15.5° C. (60° Fahr.) has been determined by experiment. Ten grammes of tar are introduced at a temperature of 40 to 50° C. into the weighing bottle, and the weight taken after cooling. Freshly boiled distilled water is then added, and the bottle kept in a bath at 15.5° C. until no further contraction takes place. The water is then adjusted to the mark, and the bottle removed from the bath and weighed. Weight of tar divided by the weight of the water displaced will give the specific gravity.

Another method of taking the specific gravity is to place about 200 c.c.'s of tar in a large covered beaker and immerse the same in warm water, the temperature of which must not exceed 50° C. This will cause entangled ammoniacal liquor to collect on the top of the tar, when it is removed either by decantation or absorbing it with blotting-paper. A portion of the dehydrated tar is then placed in a specific gravity bottle (Regnault type) and the determination taken at a temperature of 15.5° C.

Lunge estimates the specific gravity of tar by employing a weighing bottle of the shape illustrated in Fig. 72. This bottle is provided with a rill, R, 2 mm.'s wide. The specific gravity is taken as follows: The weighing bottle is first weighed empty, and then again after filling it with water at 15.5° C. The bottle is then dried, dehydrated tar poured into it until it is about two-thirds full, and the bottle, without its stopper, is then placed into hot water for about an hour, in order to disperse air bubbles. The weighing bottle and contents are then allowed to cool to a temperature of 15.5° C. and weighed. The bottle is now filled with distilled water, the stopper inserted, and any water which issues from the rill is removed, and the whole allowed to stand in a vessel containing water of a temperature of 15.5° C. for about an hour, after which the weight is again determined. The specific gravity is found by the following calculation: (*a*) Equals the weight of the empty bottle; (*b*) equals the weight of the bottle filled with water; (*c*) equals the weight

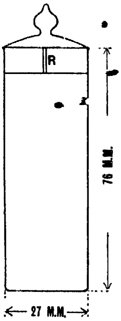

FIG. 72.—Specific Gravity Bottle for Tar Testing.

of the bottle plus the tar; (*d*) equals the weight of the bottle, tar and water; (*s*) equals specific gravity.

$$s=\frac{c-a}{b+c-(a+d)}$$

Free Carbon.—The methods of determining this material are fairly numerous, but the one which in the writer's opinion gives the best result is that devised by Hooper. This method unfortunately takes a considerable time to carry out, and on this account the writer modified it, and by doing so reduced the time to about one quarter of that which is required to carry out Hooper's test. The degree of accuracy is in favour of Hooper's test, but in the case of the writer's method the amount of error is not a very serious one, and where time is an important matter it may be used. Hooper's test is carried out as follows: Ten grammes of tar are weighed into an extraction thimble, which is then closed with a cotton wool plug and placed into a Soxhlet apparatus. The thimble and plug are previously extracted with the solvents used in the process, dried and weighed. The tar is then extracted with (*a*) 90's benzol, (*b*) 90 per cent. at 140° C. pyridine bases, and (*c*) unmineralised methylated spirit, extracting 50 times with each solvent. The thimble is then removed, dried in a steam-oven, and weighed when cold.

The following is the writer's method of determining free carbon in tar: An extraction-thimble, plug of cotton wool, and lid of filter paper are extracted, first with 98 per cent. cresylic acid, and then with 90's benzol, until extractions are colourless. The lot are then dried and tared. Ten grammes of tar are weighed into the thimble, the plug inserted, and the filter-paper cap placed over and held in position with a piece of thin platinum wire. The prepared thimble is then placed in a Soxhlet apparatus and allowed to soak in 90's benzol for a quarter of an hour, after which four extractions with 90's benzol are made. Extraction with 98 per cent. cresylic acid is then commenced, and continued until it runs away colourless, after which 90's benzol is passed through the apparatus until it shows no colour. The thimble is then removed from the Soxhlet tube, dried in a steam-oven and weighed when cold.

S. R. Church has adopted a very compact and simple extraction apparatus (Fig. 73), for use in the estimation of free carbon in tar, which in the writer's hands has given excellent results.

Sulphur.—It is sometimes desirable to estimate this substance in coal tar, and a good test is recommended by A. Renfred Myhill. A full description of the method is given in *The Gas World* for 1st February 1913. Briefly, it consists of igniting in a special manner a weighed quantity of tar with anhydrous sodium carbonate in a nickel crucible. After the fusion the mass is lixiviated with distilled water. Any sodium sulphite in solution is oxidised with bromine water and the total sulphate determined by the usual method with barium chloride and the result calculated to sulphur.

Ash.—This may be carried out by igniting carefully 5 or 10 grammes of tar in a large open porcelain or platinum crucible. Every precaution must be taken at the beginning of the operation to avoid frothing over, especially if the tar contains an excess of entangled liquor. Dehydrated tar may be used for the estimation if desired.

Testing Tar for Yield of Products.—Sometimes it is desired to determine in the laboratory the yield of products which may be obtained from a certain sample of coal tar. Laboratory tests for determining the yield of crude naphtha, light oil, creosotes, pitch, etc., are not very satisfactory, and will not give more than an approximate idea of what may be expected in the works. It is far better to erect in the works an experimental still which will deal with say 5 cwts. or even a ton, or, better, to work through a charge of say 15 or 20 tons of the tar. There are occasions, of course, when this cannot be done, and then at least *two* gallons of tar should be distilled in the laboratory. This may be carried out in a specially made copper still, cylindrical in shape, the diameter being a little less than the height, and provided with a vapour pipe, a safety valve and a thermometer, using a high-pressure gas burner to supply the

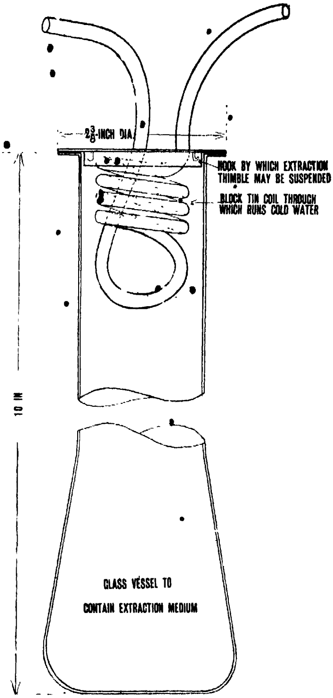
2 3/8-INCH DIA.
HOOK BY WHICH EXTRACTION THIMBLE MAY BE SUSPENDED
BLOCK TIN COIL THROUGH WHICH RUNS COLD WATER
10 IN
GLASS VESSEL TO CONTAIN EXTRACTION MEDIUM

FIG. 73.—Apparatus adopted by Church for the Determination of Free Carbon in Tar.

heat, and surrounding the still with fire-bricks. The vapour pipe of the still is connected up to an 18-inch Liebig condenser through the jacket of which, during the distilling off of the crude naphtha and the first portion of the light-oil fraction, cold water is allowed to flow. After the first portion of the light-oil fraction has come over the jacket is filled with hot water in order to prevent choking with naphthalene salts. The thermometer bulb should be in the vapours and as near the outlet of the vapour pipe as possible. Fractions are collected according to the requirements of the works manager; in a general way, however, the following may be taken as a guide:

Crude naphtha, up to . . .	170° C.
Light oil, between	170–240° C.
Middle oil, ,, ...	240–270° C.
Heavy oil, ,, ...	270–350° C.
Pitch, above	350° C.

The following table by J. M. Weiss will no doubt prove useful to tar works' chemists:

Source of Tar.	Free Carbon, per cent.	Specific Gravity at 60° F.	Coefficient of Expansion for ° F.
Water gas tar . .	1.04	1.073	0.0003750
Water gas tar . .	1.08	1.090	0.0003550
Gasworks coal tar .	16.67	1.203	0.0003125
Gasworks coal tar .	18.53	1.205	0.0003125
Gasworks coal tar .	27.50	1.249	0.0003100
Gasworks coal tar .	33.17	1.296	0.0002700
Coke oven coal tar .	8.97	1.185	0.0003375
Coke oven coal tar .	5.27	1.193	0.0003350
Coke oven coal tar .	4.04	1.178	0.0003300
Coke oven coal tar .	6.72	1.195	0.0003250
Coke oven coal tar .	6.65	1.197	0.0003125
Coke oven coal tar .	9.10	1.203	0.0003125
Coke oven coal tar .	19.06	1.258	0.0003075
Coke oven coal tar .	15.02	1.231	0.0003050

PYRIDINE

The specification issued by the German Federal Council for testing rectified pyridine bases is as follows:

Water.—This must be under 10 per cent. (it is often required that the water be not over 7 per cent.). The determination is carried out as follows: Into a special burette (see Fig. 74)

23 c.c.'s of 80° Tw. caustic soda, which must be perfectly clear, are carefully run, and if necessary after standing a short time adjusted. On to the top of the soda 25 c.c.'s of the pyridine bases to be tested are placed, a cork inserted into the neck of the burette and the contents gently shaken, after which they are allowed to stand for a short time, to separate. The ncrease in the volume of caustic soda indicates water.

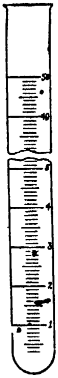

FIG. 74.—Burette for Testing Pyridine for Water.

Distillation.—Not less than 90 per cent. should distil over up to a temperature of 140° C. when 100 c.c.'s of the bases are distilled in a Wurtz distillation flask, the bulb of the thermometer being opposite the outlet tube.

Colour.—This must not be darker than a solution of 2 c.c.'s of N/10 iodine solution in one litre of distilled water.

Solubility.—The sample must be completely miscible in water to a clear solution. When 20 c.c.'s of the bases are mixed with 40 c.c.'s of water there should be no separation of oily drops.

Ammonia.—This must be absent.

The bases are required to answer the following test: Ten c.c.'s of a 1 per cent. (by volume) solution of bases must give a white precipitate with 5 c.c.'s of Nessler's solution.

Cadmium Chloride Test.—Ten c.c.'s of 1 per cent. (by volume) solution of the pyridine bases when mixed with 5 c.c.'s of 5 per cent. aqueous solution of anhydrous cadmium chloride and shaken vigorously should, almost immediately, yield a distinctly crystalline precipitate.

Titration Test.—To 1 c.c. of the bases dissolved in 10 c.c.'s of distilled water, $N/1\ H_2SO_4$ is added from a burette until a drop of the mixture gives a distinct blue colour or border on congo paper. At least 10 c.c.'s of acid must be required. The congo paper is prepared by soaking filter paper in a one per thousand solution of congo red, and allowing to dry at ordinary temperature. The paper should be prepared just before the titration is carried out.

In the new specification for pyridine bases the distillation requirements vary from those just given, thus: Up to 140° C. the bases should yield 50 per cent. and up to 160° C. 90 per cent. The titration test is carried out in the same manner, but 1 c.c. of the bases dissolved in 10 c.c.'s of water should require at least 9.5 c.c.'s of $N/1\ H_2SO_4$.

Test for Oil in Crude Pyridine.—About 250 c.c.'s of the sample are dried with 80° Tw. caustic soda. Of this dried pyridine bases 100 c.c.'s are taken and distilled in a Wurtz flask until 10 c.c.'s have come over. To this volume 90 c.c.'s of distilled water are added and the lot shaken. If the solution becomes turbid oil is indicated. In this case a further 10 c.c.'s are distilled over into another measure and 90 c.c.'s of distilled water added. After mixing, should the solution become turbid, then the batch is rejected as unsuitable and requiring further treatment.

Valuation Test of Crude Pyridine

Water.—This is carried out in the manner described under German specification for rectified bases (page 230).

Distillation.—Two hundred and fifty c.c.'s of the sample are dried by shaking with three separate quantities of 80° to 90° Tw. caustic soda, the volume in each case being about 100 c.c.'s. The dried pyridine is measured, and then placed into a 300 c.c. round-bottomed distilling flask, to which is fitted a le Bel Henninger fractionating head. This head should be provided with three bulbs, and have an overall length of about 20 inches, the distance between the bottom of the head and the outlet of the delivery tube being approximately 13 inches. The fractions are collected as follows: From drop to 140° C. (refined pyridine); from 140 to 160° C. (heavy refined pyridine); from 160 to 180° C. (heavy bases). The refined pyridine fraction is tested for (*a*) water; (*b*) oiliness; and (*c*) percentage of distillate at 140° C. Methods of carrying out these tests have already been described.

Estimation of Pyridine in Naphthas, etc.

Rough Method.—Into a 100 c.c. stoppered test mixer 50 c.c.'s of dilute sulphuric acid (1 : 2) are placed. On to this are run 50 c.c.'s of the oil to be tested, the stopper inserted, and the contents well shaken and allowed to settle. The decrease in the volume of the oil or the increase in that of the acid indicates the amount of pyridine contained in the 50 c.c.'s of oil.

A more Accurate Method.—Take 500 c.c.'s of the naphtha, place in a separating funnel and wash with 20 per cent. of diluted B.O.V. (1 acid 2 water) in two lots of 40 c.c.'s and one of 20 c.c.'s. Carefully separate the acid extracts, bulk them, place in a steam distillation apparatus, make alkaline with 40° Tw. caustic soda, and then steam distil until about one-third of the original bulk in the distilling flask has been collected. Place this distillate in a separating funnel and add 90° Tw. caustic soda until no more oil separates, allow to rest, carefully run off the subnatant alkaline liquor, dry the pyridine bases with a little 90° Tw. caustic soda, separate most of the alkali and then run the remainder with the bases into a narrow measuring tube, rinse out the funnel with a little 90° Tw. caustic soda into the tube, allow to rest, and read off volume of pyridine bases.

PITCH TESTS

The usual tests applied to pitch are: (*a*) Determination of twisting point, (*b*) ash, and (*c*) volatile matter. Occasionally it is required to estimate the specific gravity and the free carbon.

Specific Gravity.—This is estimated by the usual displacement method.

Free Carbon.—The method used for estimating this substance is the same as that employed in the case of coal tar. Of course it is advisable to grind the pitch to a powder, should the same be hard enough.

Twisting Point.—There are various ways in which this is carried out, and unfortunately this is the cause of many disputes. In the writer's opinion it is far better to rely upon a satisfactory method of estimating the volatile matter in pitch than any method of determining the twist. One method of determining the twist is that of Kohler, which is as follows: Pieces of pitch $\frac{3}{16}$ inch in thickness are placed in water at 60° C., and after this has cooled to 55° C., the pitch should be easily twisted without breaking. Pitches which answer this test are considered suitable for the manufacture of briquettes.

Another method is to take a 1-oz. sample of the pitch, soften it in warm water, and shape it between the fingers until a rod of approximately ½ inch in diameter is formed. This is allowed to harden again, and after an interval of about an hour, when immersed in water at 60° C., it should easily twist. A pitch which answers this test may be employed in the manufacture of briquettes.

Another method which is used to determine the twisting point of pitch for the manufacture of patent fuels is to immerse a piece of pitch 4 inches long and ¾ inch in diameter in water at a temperature of 60° C. for two minutes. After the expiration of this time it should bend without breaking.

A method which is used to determine the twisting point of any quality of pitch is to take a sample of the pitch, heat it (in water) sufficiently to make it pliable to the fingers, and then form a rod about 2 inches long and ½ inch in diameter. This rod is allowed to harden, and then suspended on a piece of string so that it hangs inside a beaker containing cold water. A thermometer is also suspended inside the beaker, the bulb of which should touch the rod of pitch. The beaker is placed on a piece of wire gauze, and heated with a Rose flame at such a rate that the water increases in temperature 2° Fahr. per minute. It is necessary that the water be stirred very frequently to ensure an even temperature, and the pitch occasionally lifted out and an attempt made to twist it. When it is possible to twist the sample two or three times with only a slight effort the twisting point is found.

Melting Point.—To determine this, S. R. Church recommends the following:

A ½-inch cube of the pitch to be tested is formed in a mould, care being taken not to heat the pitch unduly long or at a higher temperature than necessary. A 600 c.c. beaker is supported on a wire gauze over a bunsen burner, and hanging into the beaker are a thermometer and a copper wire (No. 12 gauge) hook. The cube of pitch is placed on this hook and suspended in the beaker at such a height that the bottom of the cube is just 1 inch above the bottom of the beaker. Water to the amount of 400 c.c. is placed in the beaker and the temperature brought to 15.5° C., and the pitch is allowed to remain five minutes in this water before heat is applied. The water is to be heated at such a rate that its temperature is raised 5° C. (9° F.) per minute. Immediately the pitch touches the bottom of the beaker the temperature is noted and recorded as the melting point of the pitch. (To prevent the melted pitch from sticking to the beaker, place a small piece of paper on the bottom and suitably weight it.) This method is employed for pitches which possess a melting point between 43° and 77° C.

For pitches with a melting point below 43° C. immerse the cube of pitch in water at a temperature of 4° C. (40° F.) for five minutes before commencing the heating.

If the pitch to be examined melts above 77° C. use cotton-seed oil instead of water, immersing for five minutes at a temperature of 15.5° C. before heat is applied.

Volatile Matter in Pitch.—There are several methods of determining this, and unfortunately there is no standard one. The writer made a considerable number of experiments, some little time ago, on the subject of the determination of volatile matter in pitch, and published many of the results in a paper read by him before the Midland Junior Gas Engineering Association.[1] The method which seemed to give the best results is as follows: A porcelain crucible 4 cm. in diameter and 2½ cm. deep, containing 2 grammes of ground pitch, is placed in a Leune furnace (such as is supplied with a Meker burner), with the lid on, the top portion of the furnace being removed. A No. 2 size Meker burner is used. The heating is extended over a period of ten minutes, and the flame kept at full blast the whole time. The furnace cover is put on after the first five minutes has elapsed. The crucible, without the lid, is then allowed to cool in a desiccator and weighed, the loss being the volatile matter.

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[1] "Investigations of Coal Tar and some of its Products." *Transactions of the Junior Gas Associations*, volume 2, page 105. *The Gas World*, March 2, 1912, p. 284.

Ash in Pitch.—This may be determined by igniting the residue left after the determination of the volatile matter, or igniting a freshly weighed-up portion. The method of estimation is quite simple and does not need any description.

CREOSOTE OIL

Much has been written on the testing of coal tar creosote, but up to the present it seems that none of the methods published have been accepted as standard ones. The usual tests to which creosote is submitted are: Determination of specific gravity; and the estimating of the percentage of water, phenols and naphthalene, and also a distillation test in order to determine the distilling range. Occasionally the percentage of free carbon and pyridine bases are estimated. Other tests which are sometimes applied are the solubility of the sample in benzol, the solubility in dimethyl sulphate, flash point, and coefficient of expansion.

Specific Gravity.—This is determined in a fairly accurate way by the use of a hydrometer, making a correction for temperature, or, better still, cooling a sample down to a prearranged temperature. It is not always possible to take the gravity of a creosote at 15.5° C., as sometimes at this temperature the material is solid or semi-solid. When the oil is liquid at 15.5° C. then it is as well that the gravity be taken at that temperature, but should the oil be solid, then it is necessary, of course, to estimate the gravity at a higher one. Sage recommends taking the specific gravity of salty creosotes at a uniform temperature of 60° C. Butterfield suggests that the gravity of salty creosotes should be determined at the temperature at which the oil is fully liquid. Often specifications state at what temperature the gravity should be taken, but seldom do they mention the method by which the determination is to be made. If it is desired to obtain a more accurate test, then the picnometer or Regnault gravity bottle should be used. Some chemists recommend the employment of a Westphal balance.

Percentage of Water.—This is determined by distilling a measured quantity of the creosote in a retort until no more water is given off. The quantity of oil taken is generally 100 c.c.'s, and the beak of the retort into which it is placed should be long and preferably surrounded by a piece of wet blotting-paper, arranged so that it is possible occasionally to re-moisten it during the distilling operation. In any case care must be taken that the distillation is not conducted too rapidly, or else some of the water will not be condensed and will escape as steam. Oil, of course, distils over with the water and sometimes does not separate well in the graduated cylinder in which it is collected. In order, therefore, to bring about a clean separation it is advisable to introduce into the cylinder about 10 c.c.'s of 90's benzol or solvent naphtha. This will hold in solution any naphthalene which may distil over, should the creosote be a very salty one, and in all cases will result in a clear reading being obtained. It is possible, of course, to estimate the percentage of water in a creosote at the same time as the test is being made for distilling range, and reference will be made to this when dealing with the fractionation of a creosote.

Phenols.—There are several methods of estimating phenolic bodies in creosote. In many laboratories it is determined by taking a measured quantity, generally 100 c.c.'s of the creosote, and placing it in a separating funnel, and then washing it with two or three successive quantities of caustic soda solution of about 40° Tw. The volumes of soda used are approximately 20 or 25 c.c.'s for each operation. The soda washings are mixed and acidified with dilute sulphuric acid (1 : 3) and the phenols which are thrown up separated and measured. Of course, should the oil be very salty, it is necessary to heat it to a temperature at which it will remain liquid and also to heat the soda a little before adding it. In cases of this kind the temperature at which the oil is measured should be noted and the tar acids separated should be measured at the same temperature. On the other hand the creosote may be weighed and the tar acids which are separated weighed also. Should the creosote be liquid at normal temperature, then a rough method for determining the tar acids is the following: Fifty c.c.'s of 40 Tw. caustic soda are placed in a 100 c.c. graduated and stoppered test mixer. On the top of this are run 50 c.c.'s of the creosote, both materials of course being put into the cylinder at the same temperature. The contents of the mixer are agitated and then allowed to stand to separate. The increase in volume of the soda or the decrease in volume of the creosote will give, when multiplied by two, the percentage of tar acids.

Another method of estimating the phenols is to distil 100 c.c.'s of the creosote in a retort and collect all that will come over up to 315° C. The distillate is heated if necessary and agitated in a separating funnel with three successive quantities of 25 c.c.'s each of caustic soda solution of a strength of 40° Tw. These soda extracts are carefully separated and mixed together, placed in a clean separating funnel and shaken out with a small quantity of ether in order to remove any entangled hydrocarbon bodies. This extracted soda solution is carefully separated m the ether and heated on the water-bath in order to drive any ether which has remained in solution. It is then cooled d rendered just acid with dilute sulphuric acid, made by mixing one part of the acid with three of water. The acidification is conveniently conducted in a separating funnel, and after allowing a period of rest for separation, the greater part of the acid sodium sulphate solution may be run off and the remainder, together with the phenols, run into a graduated cylinder, and the volume of the phenols read off. These phenols will of course contain a certain amount of dissolved water.

Church recommends distilling 100 c.c.'s of the creosote, measured at limpid point, in a Jena Wurtz flask. The flask is connected to an air condenser tube, which is kept warm by a Bunsen flame during the operation, to prevent the distillate from solidifying. The operation is continued until 95 per cent. of the creosote has been collected into a specially graduated separating funnel. The contents of the separating funnel are warmed to 60° C. in water and the volume read off. Fifty c.c.'s of a 10 per cent. solution of caustic soda are now added, and the mixture shaken well and allowed to settle. The clear soda solution is carefully removed, the oil warmed again to 60° C. and the shrinkage noted. Another 30 c.c.'s of caustic soda solution are added, shaken, separated, etc., and any further shrinkage noted. This operation is repeated until no further shrinkage takes place, and the total shrinkage of the oil is taken as the percentage of tar acids present in the original sample.

Naphthalene.—There are several methods of estimating this material in creosote, and it is very difficult to say which of these methods gives the most accurate results. A rough method of estimating this material is the following: Twenty-five grammes of the creosote are weighed in a beaker to the second decimal place, and kept at a temperature of between 50° and 60° F. for twelve hours, then at 60° F. for two hours, with constant stirring. The contents of the beaker are then carefully but rapidly transferred to a large filter paper supported in a funnel, which in its turn is supported in a water jacket, the water of which is kept at a temperature of 60° F. Draining is allowed to take place until the mass becomes fairly solid on the filter paper, when the filter paper and the contents are removed from the funnel, the top of the paper folded over and the lot placed between folds of blotting-paper and pressed under a copying press. The latter portion of this operation must be conducted very rapidly, in order to avoid any serious rise in temperature. After the pressing, the naphthalene is very carefully scraped off the filter paper into a tared dish and weighed. Sometimes the creosote is cooled to 32° F. (0° C.) for four, twelve, or twenty-four hours before separating the naphthalene as just described.

Sage recommends that the naphthalene should be estimated in the fractions of creosote distilling below 270° C., and not in the entire oil, by filtering the cooled distillate through filter cloth and pressing between bibulous paper. Mann estimates naphthalene by determining the "latent heat point" in a special apparatus. The method is fully described in the original paper by this worker.[1]

The apparatus used in Mann's method is illustrated in Fig. 75 and the test is made as follows: A portion of the sample, about 50 c.c.'s, is distilled from a small retort until incipient decomposition of the residue is observed, and the collected distillate is warmed until wholly fluid and then well mixed. The small tube A is removed from the apparatus and filled about two-thirds with the distillate. This is gradually cooled, stirring all the time with a thermometer calibrated in 0.2° C., until it becomes opaque, owing to the formation of crystals, and the temperature at which the opaqueness appears is noted. The water in the water-jacket C and the air-bath B (see Fig. 75) are then brought to a temperature two or three degrees lower than the opacity point temperature just obtained. The distillate in A is then re-melted and again cooled carefully to opacity point, when the tube is placed into B. Then the thermometer in A is adjusted so that it is quite central and the bottom of its bulb about 2 cm.'s from the bottom of the tube. The temperature will be noticed to rise slightly and then remain constant for about half a minute, after which it commences to fall. The maximum temperature reached is taken as the "latent heat point." In the original paper a curve is shown, the ordinates of which give the "latent heat point" in degrees centigrade and the abscissæ percentage of naphthalene. From this curve and the latent heat point obtained, the percentage of naphthalene in any sample may be found. It is advisable for each worker to plot his own curve in the first instance, but the following figures may be useful to those who do not wish to carry out the experimental work necessary to construct a curve:

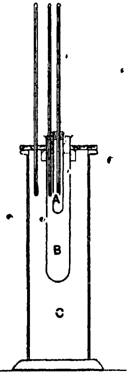

FIG. 75.—Apparatus used in Mann's Method of estimating Naphthalene in Creosote.

Actual Percentage of Naphthalene.	"Latent Heat Point."
20	30° C.
25	34° C.

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[1] "Notes on the Testing of Coal Tar Creosote," J. C. Mann, *J.S.C.I.*, June 30, 1910, p. 732.

Actual Percentage of Naphthalene.	"Latent Heat Point."
30	40° C.
35	45.5° C.
40	49.8° C.
45	52° C.

Church recommends the following method: The extracted oil from the tar acid estimation (see page 237 Church's method) is placed in a copper beaker and kept at a temperature of 15.5° C. for fifteen minutes. The mass is then filtered on a perforated funnel connected to a suction pump and sucked dry, and the naphthalene in the filter then pressed between blotting-paper in a letterpress to remove all oil, and weighed. The percentage of this material is figured on the weights of original oil as given by the specific gravity at the limpid point. Church estimates the limpid point by taking 5 c.c.'s of the creosote in a test tube at 60° C. cooling, and stirring with a thermometer, until the first crystals begin to form (limpid point). Cooling in water should be carried out if necessary.

Distilling Range. A very usual practice for obtaining the distilling range of a creosote in this country is to distil 100 c.c.'s of the oil in an 8-oz. tubulated retort, no condenser being connected to the same. The position of the thermometer varies according to individual ideas or the requirements of specifications. Some recent workers have adopted the use of a Wurtz distilling flask connected to an air-cooled condenser. In the writer's opinion the Wurtz flask method is certainly the best. The tarworks' chemist will find that specifications require the use of either a retort or flask, the size of which may vary. The position of the bulb of the thermometer is sometimes not stated; at others, in the case of a retort, it is required to be in the liquid at the commencement of the distillation, or else above the liquid, and in the case of a distilling flask, just above the surface of the liquid at the commencement of the distillation, immediately opposite the outlet tube, just below the outlet tube, and just above the outlet tube. The rate of distillation is sometimes mentioned and at others it is not. As a matter of fact there is at the present moment a great need for the adoption of a standard method of obtaining the distilling range of a creosote.[1]

Sage recommends the use of an 8-oz. retort, the upper part of the bulb of which is covered with a tin can packed with asbestos. With reference to the position of the bulb of the thermometer, this he recommends to be in the liquid at the commencement of the distillation and not more than ½ inch from the bottom of the retort. With reference to the points at which fractions should be collected, he gives the following:

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[1] "Investigations on Coal Tar and some of its Products," A. R. Warnes and W. B. Southerton, *Transactions of the Midland Junior Gas Association*, 1911-12.

(*a*) Distillate up to 210° C.
(*b*) „ between 210 to 235° C.
(*c*) „ „ 235 to 270° C.
(*d*) „ „ 270 to 315° C.
(*e*) Residue not distilling at 315° C.

With reference to these points it should be borne in mind that usually specifications detail the points at which the fractions must be taken.

Church favours the method given in the *American Railway Engineering and Maintenance of Way Association Bulletin*, No. 65. In this method a retort is used connected to an air-cooled condenser, the maximum distance from the centre of the bulb of the retort and the end of the condenser being 24 inches. The thermometer, which is a standard one, is inserted in the retort in such a fashion that the lower end of the bulb is ½ inch from the surface of the oil at the commencement of the distillation. The retort is covered with an asbestos paper cover and supported on a piece of wire gauze. It is heated with a bunsen burner surrounded by a chimney. The distillates are collected in weighed bottles, and all the fractions determined by weight, this necessitating of course the weighing into the retort of 100 grammes of the oil. When any measurable quantity of water is present in the oil, the distillation should be stopped at the point it ceases to come over; the oil is then separated from the water and returned to the retort, when the distillation should be recommenced.

Reports are made on the following fractions:

0 to 170° C.
170 „ 200° C.
200 „ 210° C.
210 „ 235° C.
235 „ 270° C.
270 „ 315° C.
315 „ 335° C.

Estimation of Free Carbon.—This comes under the head of insolubility in benzol and is determined at the same time as a solubility in benzol test. Sage recommends the following method for creosote containing no water. One hundred grammes of the creosote should be filtered whilst hot through a tared filter paper, and the filter paper afterwards washed with benzol in a Soxhlet extraction tube until the benzol runs away clear. The filter is then dried and weighed. He considers that in no case should more than 0.25 per cent. of insoluble matter be passed without comment. Should the creosote contain more than a trace of water this may be driven off first in the usual fashion, separated from the oil which comes over, the oil added to the material in the retort, and the whole lot, while warm, passed through a tared filter paper as just described.

Pyridine Bases.—These may be estimated in the creosote by shaking out say 100 c.c.'s in a separating funnel with dilute sulphuric acid (1 : 2), using three lots of about 25 c.c.'s each. The acid extractions are bulked, washed with a little ether, separated, the ether which remains in solution in the acid extract driven off on the water-bath, and the pyridine bases then thrown up by adding to the acid extract caustic soda of about 40° Tw. strength. The bases are separated and dried by treatment with 90° Tw. caustic soda and then their volume read off. Occasionally the bases are not extracted from the oil as received, but 100 c.c.'s are distilled in the retort up to 315° C. and the bases determined in the distillate.

The Dimethyl Sulphate Test.—Dimethyl sulphate will not dissolve, to any appreciable extent, paraffin or olefine hydrocarbons, but dissolves benzene and its homologues. On account of this fact, this compound has been used to determine approximately the amount of mineral oil or paraffinoid bodies in creosote. Dr Sommer recommends the following method: Four c.c.'s of the distillate are put in a 10 c.c. graduated cylinder provided with a stopper and 6 c.c.'s of dimethyl sulphate added, after which the contents are shaken thoroughly for one minute. If the distillate is not entirely soluble, a separation will take place within a few minutes, and the line of separation, being clear, can be easily read.

Flash Point.—As creosote flashes at a fairly high temperature, it is not possible to use the Abel test apparatus and obtain satisfactory results. The best apparatus to use for determining the flash point of creosote is that known as the Pensky-Marten. This apparatus consists of an oil cup with cover, to which is fitted a stirrer and thermometer. The bath is heated by a spirit lamp or bunsen burner, and the slow and regular heating of the oil is ensured by the jacket of air which surrounds the cup.

Sometimes it is necessary to obtain the open flash of creosote. This is determined by taking about 100 c.c.'s in a porcelain basin and heating it carefully with a Rose burner, stirring all the while with a thermometer. The rate of heating should be about one degree per minute, and at every degree a lighted taper should be passed near the surface of the oil. The temperature is read off immediately a flash is noticed.

Coefficient of Expansion.—The method of determining this constant is not in any way difficult. Sage recommends the following: One hundred c.c.'s of the creosote should be measured into a flask marked at 100 c.c.'s on the neck and graduated in one-tenths of a c.c. up to 106 c.c.'s. The volume should be first adjusted to 100 c.c.'s at 40 C. and the flask then warmed in a water-bath to 80° C., and the volume at that temperature measured and recorded. The factor most commonly employed is an expansion of 1 per cent. for a rise of every 22½° F., but this is not true for all creosotes or for high temperatures as well as low ones. Sage has plotted curves obtained when heating samples from 20° C. to 80° C., and the range falls within very narrow limits, his results showing that the increase in volume is 1 per cent. for each 13.3° C., or approximately one per cent. for every 24° F.

CALORIFIC VALUE OF FUELS

The importance of an accurate method of determining the heating values of various solid and liquid fuels is now considerable, and for some years the Mahler bomb calorimeter has deservedly been held in high esteem by workers in calorimetry. By means of this apparatus coals, coal-tar, creosotes and many other substances are readily examined, and the results arrived at, are of an accuracy superior to that obtainable by other and perhaps more frequently employed fuel calorimeters. Recently, the Mahler bomb has been modified by Kroeker,[1] and with this improved apparatus it is possible to correct for the inclusion of the latent heat of the water vapour, which in the furnace of a boiler, for example, escapes, its heat being consequently lost. In Kroeker's bomb there are entrance and exit tubes, by means of which a current of dry air may, after the experiment, be passed through the bomb and the escaping gases and water-vapour collected in the usual weighed calcium chloride tubes and potash bulbs, allowing of a determination of the water and, if desired, of the carbon dioxide produced in the combustion.

In the case of liquid fuels such as tar, creosotes, petroleum fractions, etc., the fuel is placed in a small platinum crucible supplied with the apparatus, and the method then carried out as for solid fuels, the ignition being made by electrical means. The results are accurate, and the apparatus is finding increasing employment at the present time. Figs. 76 and 77 show the general appearance of this calorimeter and the bomb in section.

GERMICIDAL VALUE OF COAL-TAR DISINFECTANTS

It has long been recognised that chemical methods of testing disinfectants (especially those of the coal-tar class) are of limited value in appraising their value as germicides, and in 1903 Rideal & Walker introduced their well-known "drop" method, using a standard organism (*B. typhosus*), and comparing the

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[1] The Kroeker modification of the Berthelot-Mahler calorimeter is made in England by Gallenkamp & Co., Ltd., 19 and 21 Sun Street, Finsbury Square, London, E.C., to whom the author is indebted for the loan of the illustration blocks on pages 243 and 244.

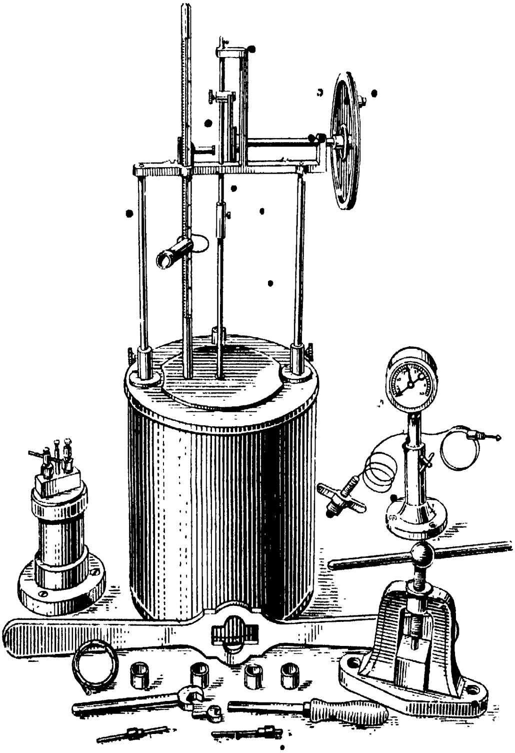

FIG. 76.—Berthelot-Mahler Bomb Calorimeter with modified Bomb by Dr K. Kroeker.

diluted disinfectant with a solution of pure phenol. In spite of much adverse criticism, this method remains the standard procedure for testing disinfectants against a "naked" organism. To perform the test accurately, many precautions have to be taken, and only an expert in its use can obtain trustworthy results.

Briefly, the method consists in shaking together 5 drops (=0.5 c.c., delivered from a special pipette, of a 24-hours-old broth culture grown at 37° C. of *B. typhosus*, or other standard organism selected for the purpose) with 5 c.c. of a known dilution of the disinfectant in sterile distilled water and taking out from the mixture, for subcultivation in broth, a large drop of the liquid every 2½ minutes up to 15 minutes. The subcultures are incubated at 37° C. for 48 hours, when they are examined for signs of growth, and the results carefully noted. A tabulated statement of these results must show a positive result (growth) in the first column (2½ minutes) and a negative result (no growth) in the last (15 minutes). A standard 1 per cent. solution of pure phenol is tested side by side with the disinfectant. Four dilutions of a disinfectant can be tested with the diluted phenol at the same time, a special tube-rack holding these dilutions and thirty tubes of broth (6 sets of 5) being used for convenience of working. The efficiency of the disinfectant is expressed in terms of the standard phenol solution, and when a dilution of the disinfectant has been found which has the same germicidal value in the above test as the standard phenol solution, the former is divided by the latter, when the Rideal & Walker coefficient is obtained. Thus if a 1 in 70 solution of a disinfectant has the same action as a 1 in 80 solution of phenol, the tested disinfectant is not so strong as phenol, and the coefficient is 70/80 or 0.87 (R.W. coefficient).

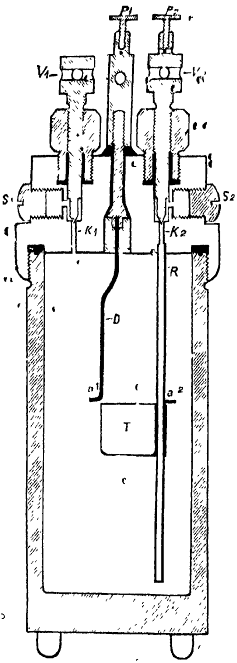

FIG. 77.—Section of Bomb with Kroeker's Modification, showing Platinum Crucible.

A number of precautions must be taken, chief amongst which are: The temperature must not vary more than 2° C. during the carrying out of the tests; pipettes, tubes and measures, etc., must be sterile; the solidifying point of the standard phenol used for making the test solution must not be below 40° C.—phenol containing cresols is inapplicable; the broth used for cultures should be a "Lemco" broth of prescribed composition, standardised to a +1.5 per cent. reaction (when *B. typhosus* is the test organism).

Further details for carrying out this important test will be found in Moore and Partridge's *Aids to Bacteriology*, third edition, 1916, pp. [illegible] *et seq.*

It will be seen that in the Rideal-Walker test, the culture organism is exposed to the disinfectant in a "naked" condition; that is to say, the conditions of the test do not approximate to the actual circumstances of practical disinfection, where generally the disinfectant comes into contact with pathogenic and other organisms together with much organic matter of varying nature. For this reason, it has been suggested that extraneous organic matter should always be present in the test. It is, however, a matter of some difficulty to prescribe a standard uniform organic addition in suitable amount; and for this reason the Rideal-Walker test in its accepted form should always be carried out without added organic matter, this material being added if desired in another series of tests made separately. The addition of any organic matter tends to lower (sometimes appreciably) the carbolic acid coefficient of the disinfectant.

BENZOL

Specific Gravity.—This is determined with an ordinary specific gravity hydrometer after cooling the benzol to 15.5° C. Some chemists take the gravity at the temperature of the laboratory and correct it by adding .001 to the specific gravity reading for every 2° F. above 60° or subtracting the same figure for every 2° F. below 60°. This method is not to be recommended, as the factor is not accurate for all temperatures. The best method of estimating the specific gravity of this material is to use the Regnault specific gravity bottle.

Distillation.—For making rough works' tests, such as determining the percentage given off from a sample obtained from the worm end of the benzol still, an 8-oz. retort is used, connected to a Liebig condenser and supplied with a benzol testing thermometer, which is graduated from 70° to 130° C. in one-fifths of a degree. The length of the Liebig condenser is about 30 inches and the condenser tube about 1 inch wide. The thermometer is fixed so that the bottom of the bulb is about $\frac{3}{8}$ inch from the bottom of the retort. A Rose burner is used to heat the contents of the retort, and the distillation should proceed at the rate of about two drops per second. It should be added that benzol is tested before delivery for its percentage at 100° C. or 120° C., according to quality, in the same apparatus.

Pyridine in Benzol.—Badly made benzols may contain pyridine bases, and it is advisable to test for these if the sample is suspected. The test may be carried out as follows: One hundred c.c.'s of benzol are agitated with four parts of a 10 per cent. solution of sulphuric acid in a separatory funnel. After a thorough shaking, the contents of the funnel are allowed to rest and the acid solution run off from the bottom into a distilling flask and then made alkaline with caustic soda. The flask is connected up to a Liebig condenser and a steam generating apparatus, and the contents submitted to steam distillation until about one-third of the volume in the distilling flask has come over. When the distillate is cold 90° Tw. caustic soda is added, and the bases which rise to the surface, if sufficient, are carefully separated and measured.

Total Sulphur in Benzol.—The following method, if carefully conducted, will give very satisfactory results. It is a modification of a test published by Irwin. Into a 2-oz. spirit lamp provided with the usual unplaited wick, which is kept very short on the burning side, are placed 2 c.c.'s of benzol, which should be measured in from a burette at 60° F. On the top of the benzol are poured 20 c.c.'s of 90 per cent. alcohol B.P., and the lot carefully mixed. The spirit lamp is placed under the trumpet stand of the Metropolitan Gas Referees' sulphur test apparatus, the burner portion projecting through the centre hole where in the ordinary course the gas burner should be. The Gas Referees' apparatus is prepared in the same fashion as when determining the sulphur in a sample of coal gas; that is, a little powdered ammonium carbonate is sprinkled over the top layer of glass marbles in the condenser and a few small lumps placed round the burner top. The lamp is lit immediately it is placed under the trumpet and allowed to burn at such a rate that it will take about 1¾ hours to consume the contents. Immediately the lamp goes out it is removed, and a further 5 c.c.'s of alcohol placed in it, and this burnt under the apparatus until the lamp goes out, the time taken being about 20 minutes. The flame should be almost colourless at the end of the process. The whole of the apparatus is washed down with distilled water in the usual fashion into a beaker, and the sulphur estimated in the usual way and if desired calculated to CS_2. There are other ways of estimating CS_2 in benzol, such as the phenylhydrazine test and the copper xanthate method. The reader is referred to *Allen's Commercial Analysis* and other authorities on analytical matters for these tests.

Estimation of Fatty Hydrocarbons.—This test is sometimes applied to benzol, especially when it is intended for the manufacture of nitro-compounds. Lunge gives the following process:

One hundred grammes of benzol are nitrated with 125 grammes of sulphuric acid, specific gravity 1.84, and 125 grammes of nitric acid of a specific gravity of 1.5, at a temperature not exceeding 30° C. The crude nitro-benzol is separated from the acid liquid in a separating funnel, neutralised with caustic soda, and distilled by means of steam until a sample of the distillate sinks in water. The distilled oil is separated from water and placed in a 50 c.c. stoppered and graduated cylinder, and to this 15 to 40 c.c.'s of the mixed sulphuric and nitric acids, made as before described, are gradually added with occasional shaking until the volume of the oil ceases to diminish. Any unchanged benzene and toluene are dissolved in the acid mixture, and the fatty hydrocarbons, being unacted upon, will float on the top and their volume may be read off. This volume is calculated as amounting to 60 per cent. of the fatty hydrocarbons actually present, and the test is only made if there is reason to expect a somewhat large proportion of these substances.

VALUATION OF CRUDE NAPHTHA FOR YIELD OF BENZOL, ETC.

Crude naphtha and crude benzol are examined for the yield of light products in the chemical laboratory by the following method: Five hundred c.c.'s. of the oil are placed in a distilling flask fitted with a 5-bulb Glinsky or le Bel Henninger distillation head. The delivery tube of this latter piece of apparatus is connected up to a Liebig condenser. Distillation is commenced and the amount of distillate which comes over below 200° C. is collected and the percentage read off. This distillate is then washed, first with about 60 c.c.'s of 60° Tw. caustic soda, using a separating funnel. The alkaline liquor which separates is carefully removed and the shrinkage in the oil carefully measured. The oil is then washed once or twice with water, care being taken of course to prevent loss of oil when separating the water, and then agitated with B.O.V. of about 140° Tw., two washes of 2½ per cent. being given. The acid liquor which separates is carefully removed, and the oil then given one or two water washes, after which it is washed with 50 c.c.'s of 20° Tw. caustic soda and then with one wash of water. It is then allowed to rest to separate the last traces of water, and the shrinkage of oil carefully measured. The entire quantity of the washed oil is now placed into a distilling flask fitted with a Glinsky or le Bel Henninger head, as just described, and the following fractions are collected:

Drop to 100° C.		equals	90's benzol.
100	„ 120° C.	„	50's–90's benzol.
120	„ 160° C.	„	solvent naphtha.
160	„ 190° C.	„	heavy solvent.

The bottoms are also measured. It should be added that the volumes of these fractions will give only an approximate idea of what is obtained in the works, but at the same time they form a useful guide when buying say crude benzol or crude naphtha.

In the case of crude naphtha the percentage at 120° C. is often determined by using a retort and condenser as just described under benzol tests, and of course the specific gravity is always taken. It is advisable to test the crude naphtha for tar acids and basic bodies by the methods already given.

NAPHTHAS

Distillation.—The various qualities of naphtha are tested in a similar apparatus to that used for benzol, whether it is required to control the working of the naphtha still or the quality of the products to be offered for sale. A special thermometer is used, graduated from 90° to 200° C. in half degrees, and this is placed in the retort in a similar position to that occupied by the benzol thermometer. The drop point and the percentage at 160°, 170° or 200° is read off according to the quality of the naphtha.

Specific Gravity.—This is taken by a hydrometer or in the Regnault specific gravity bottle.

Flash Point.—This is determined in the Abel test apparatus, in a similar fashion to that used for the determination of the flash point of petroleum.

Pyridine Bases and Tar Acids.—It is advisable to examine solvent naphthas for pyridine bases and also for tar acids. The latter substances are estimated as already described (see page 236), and the former (unless suspected to be present in more than traces, when the test described under benzol is used) by the following method, which is known as the Weber test for pyridine: Shake out 100 c.c.'s of solvent naphtha with 100 c.c.'s of distilled water in a separating funnel. Take about 15 c.c.'s of the water extract and add to it 1 c.c. of a 10 per cent. solution of copper sulphate. Bring the mixture to boiling point. It is required that no turbidity occurs. According to Weber, if the mixture remains clear the solvent naphtha is free from pyridine, or the amount it contains does not reach more than one part in 1500 parts of solvent naphtha. A very faint turbidity after standing 30 minutes will be equivalent to approximately .06 per cent., and a pronounced bluish white tubidity to 0.1 per cent. If the quantity of pyridine exceeds 0.1 per cent. a copious precipitate results, and should 0.3 per cent. be present a dense precipitate is at once produced. If the solvent naphtha be required for rubber works, this test often has to be used, and also the following: Twenty-five c.c.'s of R.O.V. and 75 c.c.'s of the solvent naphtha are placed in a stoppered and graduated test mixer. The mixture is well agitated and allowed to rest. The R.O.V. should not increase in bulk more than 4 c.c.'s, making a total of 29 c.c.'s, and the colour should not be more than a deep orange.

Another test often used for pyridine is to extract 50 c.c.'s of the solvent naphtha with 50 c.c.'s of B.O.V. in a separating funnel, allow to rest, separate the acid extract, neutralise with fairly concentrated caustic soda, say 60° Tw., and see whether pyridine can be detected by the sense of smell.

VALUATION OF LIGHT OIL, ETC.

There are several methods of testing light oil in order to obtain an idea of the yield of light products which may be expected in the works. One of the methods is the following: Five hundred c.c.'s of the light oil are placed in a distillation flask fitted to a 5-bulb Glinsky or le Bel Henninger distillation head and Liebig condenser. The flask is heated with a bunsen burner, and all the distillate which comes over below 200° C. collected and the percentage read off. This distillate is washed first with about 60 c.c.'s of 60° Tw. caustic soda, and then once with about the same volume of clean water, after which the loss, due to the alkaline wash, is carefully measured and the percentage noted. It is now washed with 5 per cent. of B.O.V. in two 2½ per cent. quantities, and then three times with about 60 c.c.'s of water, after which an alkaline wash is given, using about 50 c.c.'s of 20° Tw. caustic soda, and finally a wash with 50 c.c.'s of clean water. The loss in volume of oil is carefully measured, and the washed distillate is then placed in a distillation flask and distilled up a fractionating head, using one or other of the types just mentioned, and the following fractions collected:

1. Drop to 100° C. equals 90's benzol.
2. 100° ,, 120° C. ,, toluol.
3. 120° ,, 160° C. ,, solvent naphtha.
4. 160° ,, 185° C. ,, medium heavy naphtha.
5. 185° ,, 200° C. ,, heavy naphtha.

The results are calculated on the original oil and tabulated as follows:

Distillate above 200° C.	per cent.
Loss by soda and water washing . .	,,
Loss by acid, soda and water washing .	,,
90's benzol	,,
Toluol	,,
Solvent naphtha	,,
Medium heavy naphtha	,,
Heavy naphtha	,,

Specific Gravity.—This is taken by one of the methods already described.

Tar Acids and Pyridine Bases.—The processes for estimating these substances have been described already.

CRESYLIC ACID

Specific Gravity.—This constant is determined either by a hydrometer or specific gravity bottle.

Water.—This material is usually estimated by distilling carefully 100 c.c.'s of the sample in an 8-oz. retort until all the water and 10 c.c.'s of oil have been collected in a measure. A little benzol is then added to the contents of the measure, with shaking, and the mixture allowed to stand in order to enable the water to separate, when a clear reading may be obtained.

Distillation.—This test should be conducted in a Wurtz or distillation flask connected to an air condenser. The percentage of distillate is read off, as a rule, at the following points: 194° C., 196° C., 198° C., 200° C., 202° C., and 204° C.

Naphthalene and Neutral Oils.—This is not an easy test to carry out, and at the best is only approximately accurate. Twenty grammes of the sample are taken and placed in a separating funnel. The beaker in which the 20 grammes were weighed is rinsed out with 100 c.c.'s of 15 per cent. caustic soda and the rinsings added to the cresylic acid in the funnel. The lot is well shaken, and when the acids have dissolved 100 c.c.'s of distilled water are added with thorough agitation. If a clear solution results, then naphthalene and neutral oils may be considered absent, but in the case of marked turbidity, the mixture is extracted with light petroleum ether, which is dry at 75° C., the extract carefully separated, run into a weighed beaker or flask, the ether cautiously evaporated off on a water-bath and the residue weighed.

In cases in which the cresylic acid contains a fairly large quantity of oil and naphthalene, the following rough test may be used: Into a 100 c.c. stoppered test mixer 40 c.c.'s of 60° Tw. caustic soda are placed, and on the top of this 40 c.c.'s of cresylic are carefully poured. The two substances are thoroughly mixed and then allowed to cool down to 60° F., after which 5 c.c.'s of benzol are added and the lot shaken up. The contents of the test mixer are now allowed to stand in order that the benzol may separate, together with any oil and naphthalene which it has dissolved; the increase in volume of benzol may be taken as oil. The writer does not altogether approve of this test.

Tar Acids in Cresylic.—If it is desired to estimate these, the following method may be used: One hundred c.c.'s of the sample measured at 60° F. are placed into a separating funnel and about 100 c.c.'s of 60° Tw. caustic soda, added to the same, and the lot well shaken until the cresylic has dissolved. The solution is then extracted with light petroleum ether, the ether extract carefully separated, and the cresylate of soda filtered through a little glass wool into a large beaker. It is brought up to the boil and kept at this point for about two minutes, after which it is allowed to cool down. It is then placed in a separating funnel, the beaker being rinsed out with a little water and the tar acids thrown up by the addition of dilute B.O.V. A sufficient length of time is given for the tar acids to separate properly, when the subnatant sulphate of soda liquor is separated, and the tar acids run into a measure and the volume read off.

Sulphuretted Hydrogen and Sulphur Compounds.—During the manufacture of cresol it is necessary to test it for sulphur

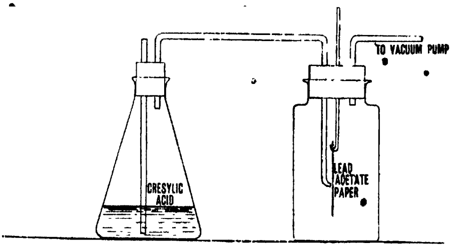

FIG. 78.—Apparatus used in Testing Cresylic Acid for Sulphur.

compounds, and it is also advisable to examine samples which are being purchased for the same substances. The method generally used is to place about 50 c.c.'s of the cresol in a flask fitted with air inlet and outlet tubes, the inlet tube dipping into the cresol. The outlet tube is connected to another flask, which in its turn is fitted to a filter pump. In this flask a piece of lead acetate paper is suspended in such a position that it hangs over the air inlet tube. Air is aspirated through the cresol by means of the filter pump, and during its passage through the second flask it comes in contact with the acetate paper. Should sulphur compounds be present the paper will turn brown or black. A good sample of cresylic will not blacken an acetate paper after 15 minutes. Fig 78 illustrates the arrangement of the flasks, etc.

META-CRESOL—CRESYLITE TEST

There is a special grade of cresylic acid manufactured which contains a considerable quantity of meta-cresol. This material is used for the manufacture of trinitro-meta-cresol. There are two methods of testing this substance, one of which is known as the short test and the other as the long test. They are carried out as follows:

Short Test.—Ten grammes of the cresol are placed in an Erlenmeyer flask and 15 c.c.'s of 66° Bé. sulphuric acid are added. The lot is well agitated, and then heated for one hour in a steam-oven After this the sulphonated mixture is poured into a 1-litre flask and thoroughly cooled under a water-tap. Into the Erlenmeyer flask in which the cresol was sulphonated 90 c.c.'s of 40° Bé. nitric acid are placed and thoroughly shaken until the sulphonated material adhering to the flask sides is rinsed off with the acid. It is then cooled a little and transferred rapidly to the contents of the litre flask. The lot is now vigorously shaken. In a few minutes reaction will take place. The mixture is now allowed to stand until the reaction is finished, when it is emptied into a large porcelain basin containing 40 c.c.'s of cold water. The flask is rinsed out with another 40 c.c.'s of cold water and the rinsings added to the contents of the basin, after which the lot is allowed to remain until the trinitro-meta-cresol crystallises out. It is then filtered through an ordinary filter paper, the crystals dried in a steam-oven at 95 to 100° C., and weighed; the result multiplied by 10 equals the cresylite test.

Long Test.—A retort of a capacity of 1 litre is fitted with a cylindrical dropping funnel, provided with a stop cock, holding about 50 c.c.'s. The retort is placed in a spherical sand bath, about 14 cm.'s in diameter. The operation must be conducted in a fume cupboard. Into the retort 50 grammes of nitric acid of 40° Bé. strength are placed and gently warmed to a temperature of 80° C. In the meantime 50 grammes of the sample of cresol are mixed with 125 grammes of sulphuric acid and allowed to stand for an hour. After this time has elapsed the contents of the flask are run into the dropping funnel and the flask inverted over it in order that it may thoroughly drain. The sulphonated cresol is allowed to drop into the nitric acid at such a rate that the whole of the contents of the dropping funnel will take between 1½ to 2 hours to run into the acid. The temperature must be kept at 80° C. the whole of the time and regular ebullition maintained. Red vapours are given off, and should these vapours whiten towards the finish, the test must be repeated with a larger quantity of nitric acid. The nitric acid should not be in great excess as the trinitro-meta-cresol is appreciably soluble in mother liquor charged with nitric acid. Immediately the whole of the sulphonated cresol has dropped into the nitric acid, the gas flame is removed and 20 minutes allowed to lapse, after which the contents of the retort are poured into a large porcelain basin containing 400 c.c.'s of cold water. The mixture is then left to cool for 24 hours, and the crystals which form are carefully separated from the mother liquor by decanting the latter into a filter funnel provided with a perforated filter disc and covered with round filter paper. The mass of crystals in the basin is melted in 200 c.c.'s of water, allowed to cool, the mother liquor removed as just mentioned, the crystals broken up, allowed to drain, dried at 50° C., weighed, and multiplied by two.

CARBOLIC ACID

Specific Gravity.—This constant is determined by a hydrometer or specific gravity bottle.

Water.—This is generally determined during the carrying out of the crystallising test.

Solubility.—The sample is required to answer the following: Fifty c.c.'s of the crude carbolic acid must be completely soluble in 100 c.c.'s of caustic soda of a specific gravity of 1.10.

Crystallising Point.—There are one or two methods of carrying this out, but that generally used for the buying and selling of crude carbolic acid is the following; and it is known in the trade as Lowe's method: Into an 8-oz. tubulated retort, having a neck about 15 inches long, 100 c.c.'s of the crude acid to be tested are placed. No condenser is connected to the beak of the retort, and the distillation is so regulated that no vapours are given off, and the operation occupies about two hours. Clean, dry, graduated cylinders must be used for the collection of the distillates. Into the first receiver 10 c.c.'s of oil and all the water (which latter shall not exceed 15 c.c.'s) are collected. The next 62½ c.c.'s are collected in the second receiver, well mixed, and cooled slowly to near the expected crystallising point. A small quantity of pure crystals is then added, and the cooling continued—stirring all the time. When the distillate is crystalline throughout, the thermometer (a Fahrenheit graduated in one-tenths of a degree) is read; and the figure indicated is taken as the crystallising point of the crude acid. It is often necessary to employ a cooling solution, and when this is the case, care must be taken that the temperature of this solution is not more than 2° F. below that at which the sample is expected to crystallise.

With low crystallising acids—*e.g.* 50's and 45's, etc.—the determination of the point at which the first crystals appear is, unfortunately, rather a tedious process, and with the object of rendering it easier and quicker, the writer and his assistant[1] made numerous experiments with a modified method, with very encouraging results. Up to the collection of the 62½ c.c.'s of acid in the second receiver, the process is identical with Lowe's. The modification consists in just half filling a test tube 5 inches long by ⅝ inch in diameter with the well-mixed distillate, cooling while stirring until the contents of the tube are crystalline throughout—adding a small crystal of pure acid, if necessary—removing from the cooling mixture, and stirring slowly, at a temperature of about 60° F., until all crystals disappear. This point is called the liquefying point; and if 2.5 is deducted from the figure obtained, the crystallising point of the acid is found. This figure was arrived at by taking the average of fifty experiments, the highest difference being 3.0 and the lowest 2.2.

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[1] "Investigations on Coal Tar and some of its Products." *English Junior Gas Associations' Joint Proceedings*, 1911-12, Sec. M, pp. 105-125. *The Gas World*, March 2, 1912, p. 284.

A handy method for use in the works when making mixings is the following, and this method may be termed a short test: One hundred c.c.'s of the crude carbolic are distilled in an 8-oz. retort until all the water and 10 c.c.'s of the oil has come over. A further 20 c.c.'s of the tar acids are now collected in a perfectly dry cylinder, the crystallising point determined, as already explained under Lowe's test, and from the figure obtained 8 is deducted, when the result will indicate approximately the actual crystallising point. Another short test is the following: Into a three-bulb Ladenburg flask of 150 c.c.'s capacity, 80 c.c.'s of crude carbolic are placed. The flask is connected to a 12-inch Liebig condenser, the jacket of which is filled with water, but no flow is maintained. All the water is distilled off, and 8 c.c.'s of the oil. Then into another perfectly dry receiver 50 c.c.'s of the tar acids are distilled and the crystallising point taken. If the figure 1 is deducted from the result, the crystallising point obtained by the long test is found approximately.

Tar Acids in Phenolate.—In order to control the working of the carbolic (and also the cresylic) plant, it is necessary to determine the amount of tar acids in the phenolate. This can be done rapidly by the following method: One hundred c.c.'s of the phenolate are placed in a separating funnel and dilute B.O.V. (1 : 2) is added until the mixture is strongly acid to litmus paper. The lot is allowed to stand for a few minutes in order that the tar acids may separate completely, after which the sodium sulphate liquor is removed carefully and the volume of the tar acids measured.

ESTIMATION OF CARBOLIC ACID IN CRUDE PHENOLS

Mm. René Masse and Henri Leroux have presented to the French Academy of Sciences a note upon carbolic acid and the estimation of this in crude phenols from tar. The method still in use for the preparation of carbolic acid is that devised by Laurent in 1841, namely, (1) Separation of phenols from creosote oils by shaking up with soda, (2) acidification to set free the crude phenols, and (3) the extraction of the carbolic acid by rectifications and crystallisations. Good crude phenol, free from naphthalene, contains water, carbolic acid, orthocresol, metacresol, paracresol, xylols and homologues, and phenolic tarry matters. The chemical properties of carbolic acid and the cresols are so nearly related that there is no simple reagent which can separate them; thus Koppeschaar's bromine method will not work if both orthocresol and metacresol be present. The physical properties, on the other hand, do enable us to discriminate. The boiling points of phenol (carbolic acid), orthocresol, metacresol and paracresol at 760 mm. barometric pressure are respectively 183°, 190.8°, 202.8° and 201.8° C.; those of the xylols are 220° and 225°. By fractionally distilling the crude phenol up to 203° C., and then fractionally distilling the fraction obtained between 180°-203° C. up to 198° C. (as described in the next paragraph), we can find the quantity of carbolic acid in each of these fractions by determining their respective crystallising points. Commercial carbolic acid, called 40° to 42°, has a melting or solidifying point slightly above 40° C.; commercially pure carbolic acid has a melting point of 40.85° C. When we add cresols to pure carbolic acid the melting point falls steadily, and that to very nearly the same extent whatever be the relative proportions of the three cresols, so long as the cresols added do not exceed 33 per cent. of the whole. The melting point of the mixture thus depends on the percentage of carbolic acid, and the curve of melting points is a straight line joining the two points phenol 100 per cent., melting point 40.85° C. and 66 per cent., 21° C. This is the basis of the following working method:

Three kilograms of crude phenol are put in a still with copper vessel of 4 litres and a Vigreux column of 24 inches. The distillation is maintained at 7 to 8 c.c. per minute, and the following fractions are taken: (*a*) up to 180° (=water and phenols); (*b*) 180° to 203°; (*c*) above 203°, 100 c.c. only. To (*a*) add enough chloride of sodium (35 per cent.) to precipitate the phenols contained in it; decant these phenols and add them to (*b*). Put (*b*) into a flask of sufficient size; wash out the vessels with liquid (*c*) and add this to (*b*). The liquid (*b*), with its additions, is now fractionally distilled at 4 c.c. per minute. The fractions taken are from 250 to 300 grammes each, until the temperature of the vapours reaches 198° C. The solidification point of each fraction is then determined. A test-tube determination gives a rough indication; but with 30 to 40 grammes, allowed to cool slowly until supercooled by 1° or 2°, the addition of a trace of crystallised carbolic acid determines crystallisation and the temperature goes up to the true melting point. If in the test-tube trial the required temperature is below 21° C., add carbolic acid in known quantity sufficient to bring the percentage of carbolic acid above 66.

This method enables the carbolic acid in a crude phenol to be estimated within 1 per cent., which is as near as could be expected with so complex a mixture as crude phenol.

ANTHRACENE TESTS

Crude and refined anthracenes are tested for the percentage of actual anthracene by what is known as Luck's test. The following materials are required: *Chromic acid solution.*—This is made by dissolving 150 grammes of chromic acid (CrO_3) and 100 c.c.'s of glacial acetic acid in 100 c.c.'s of distilled water. *Fuming Sulphuric Acid Mixture.*—This is prepared by mixing equal parts of pure sulphuric acid of a specific gravity of 1.84 and Nordhausen sulphuric acid of a specific gravity of 1.92.

The test is carried out as follows: One gramme of the sample is placed in a 1-litre boiling flask, and to it is added 45 c.c.'s of glacial acetic acid. The flask is connected to an air-cooled reflux condenser, and then placed on a sand-bath and the contents boiled until the anthracene is dissolved. In the meantime 23 c.c.'s of the chromic acid mixture are placed in a dropping funnel, the stem of which is inserted into the top of the reflux condenser. As soon as the anthracene is dissolved in the acetic acid, the chromic acid mixture is allowed to drop into the solution at such a rate that it will take two hours for the whole of it to run out of the dropping funnel. After all the chromic acid solution is in, the mixture is boiled for a further two hours and then allowed to stand for twelve hours. It is then diluted to 500 c.c.'s with distilled water and allowed to remain at rest for one hour, after which it is filtered through a hardened filter paper and washed with (*a*) 200 c.c.'s of cold water, (*b*) 300 c.c.'s of boiling water, (*c*) 300 c.c.'s of 2½° Tw. caustic soda, and (*d*) 300 c.c.'s of boiling water. The precipitate is now washed into a tared porcelain basin, dried on a water-bath, and finally in a steam-oven, and then weighed. The weight obtained gives a figure which when multiplied by 85.6 is recorded as the common test. To the material in the basin is now added ten times its weight of the fuming sulphuric acid mixture, after which it is heated on a water-bath until the whole mass has crystallised. This will take between 10 to 15 minutes. It is then stood in a damp place overnight, and the following morning diluted with 200 c.c.'s of cold water, after which it is filtered through a hardened filter paper and washed with boiling water, soda, and boiling water, as before. The precipitate of quinone is then washed into a tared porcelain basin, dried in a steam-oven and weighed. After weighing, the basin and its contents are gently heated in order to volatilise the quinone, and when cold the basin and ash are re-weighed. The difference between the first and the second weighings gives the weight of anthraquinone, and this multiplied by 85.6 will give the percentage of actual anthracene in the sample.

Material Insoluble in Benzol (Sand, Dirt, etc.).—Five grammes of anthracene are transferred to a previously weighed extraction thimble, placed in a Soxhlet extraction apparatus and extracted with benzol in the usual way until the benzol leaves the apparatus colourless. The thimble is then removed, freed from benzol in a steam-oven, cooled, and weighed. The increase in weight of the thimble indicates insoluble matter. It is necessary of course to cover the extraction thimble with a piece of filter paper, the edges of which may be bound with platinum wire, or else use a plug of cotton wool.

Paraffin in Anthracene.—This may be estimated as follows: Ten grammes of the sample are weighed into a large beaker and to it are added 108 c.c.'s of concentrated sulphuric acid. The mixture is heated on the water-bath until all the anthracene is dissolved. Then it is cooled and poured into 400 c.c.'s of cold water contained in a 1000 c.c. separating funnel. The mixture is allowed to cool and is then extracted twice with light petroleum ether (dry at 75° C.). The petroleum ether extracts are bulked and washed in a separating funnel, first with half its bulk of 5° Tw. caustic soda, and then four times with one-eighth of its bulk of cold concentrated sulphuric acid, and after this with cold water until free from acid. It is then allowed to settle, any water which separates removed, and then transferred to a tared flask, and the ether distilled off and the residue weighed.

EXAMINATION OF CAUSTIC LIQUORS, SPENT LIQUORS, AND LIME MUD IN CONNECTION WITH THE CO_2 PROCESS FOR MANUFACTURING TAR ACIDS

Spent Liquors.—It is essential that the causticised spent liquors be kept up to a standard strength as regards the percentage of actual caustic soda, and owing to the fact that impurities, sometimes to a moderately large extent, are always present in these liquors, it is not possible to control the strength with any degree of accuracy by the use of a hydrometer. It is necessary, therefore, to titrate the spent liquor with a standard acid solution for the amount of alkali present (calculated to sodium carbonate, Na_2CO_3), and then to add an amount of soda ash to the bulk of spent liquor in the causticisers to bring up the strength to the normal. The best results seem to be obtained by causticising spent liquor which contains 10 grammes of Na_2CO_3 per 100 c.c.'s. The writer advises tarworks' chemists who have control of a CO_2 plant for tar acid recovery to work out a table for themselves, showing the amount of soda ash required for each causticiser as indicated from the results obtained from his analysis, allowing of course for the impurities in the soda ash used. For instance, assuming the spent liquor on analysis showed 9.8 grammes of sodium carbonate per 100 c.c.'s, then the material in the causticiser would require approximately 2.8 lbs. of soda ash (58 per cent., alkali) for every 100 gallons. The titration is carried out in the usual manner, but the liquor, as it is generally very dark, must be well diluted, and an indicator such as lacmoid or cochineal should be used.

Estimation of Caustic Soda in Lime Mud.—This may be rapidly estimated with a fair degree of accuracy by the following method: Twenty grammes of the mud are weighed in a 250 c.c. beaker and 100 c.c.'s of hot water poured on top of it. A gentle stream of carbonic acid is passed into the mixture for about ten minutes, after which it is boiled, filtered, and the precipitate washed, the filtrate and washings being run into a 200 c.c. measuring flask. The contents of this flask are allowed to cool to 60° Fahr. and then made up to 200 c.c.'s with distilled water and well mixed. An aliquot portion (say 25 c.c.'s) is then removed by means of a pipette and titrated in the usual fashion, calculating to NaOH.

Estimation of Actual Caustic Soda in a Dark-coloured Causticised Spent Liquor.—As the causticised spent liquor is always very dark in colour, it is not possible to estimate the amount of caustic soda in the presence of carbonate by the method of double titration, which is used in the case of commercial caustic sodas. The following method gives very satisfactory results: Fifty c.c.'s of the dark-coloured liquor (free from lime precipitate) are brought up to a temperature of 100° C. Barium chloride solution at a temperature of 95° to 100° C. is now added until no more precipitate forms. The lot is filtered while hot into a 250 c.c. measuring flask, the precipitate and filter paper washed with a little boiling water, and when cold the filtrate and washings are made up to the mark with distilled water, and an aliquot portion taken and titrated for caustic soda in the usual fashion.

TESTING THE COKE FURNACE GASES FOR USE IN THE CO_2 TAR ACID PROCESS

It is advisable that frequent tests of the gases be made as they leave the coke furnace, in order to control the efficient working of the CO_2 tar acid plant. The most convenient apparatus to use for this purpose is the Orsat. The manipulation of this apparatus is so simple that an intelligent works plant man may be taught how to use it satisfactorily in a very short time. It is advisable to estimate the carbon dioxide, oxygen and carbon monoxide in each examination.

Coke.—The deliveries of this material should be examined for the amount of water, ash, and sulphur, and sampling before analysis must be carried out with care by one of the approved methods. To estimate the water, twenty grammes of the ground coke are heated in an air oven to a temperature of 110° C. until of constant weight. The ash is determined by burning off two grammes of the coke in a platinum dish and weighing the residue. Sulphur in coke may be estimated by Stock's method, which is as follows: One gramme of coke in fine powder is mixed in a round-bottomed platinum capsule with approximately one gramme of half-hydrated caustic lime, moistened with water (1 c.c.), rapidly dried, and then heated in a muffle to bright redness until all carbon has disappeared. The mass is allowed to cool, transferred to a beaker, twenty c.c.'s of cold distilled water and five c.c.'s of bromine water added, and then 7½ c.c.'s of pure strong HCl, after which the lot is boiled for five minutes. The contents of the beaker are then passed through a filter paper (filtrate must be bright), the beaker and the filter being well washed and the washings added to the filtrate. The filtrate and washings are then boiled, and whilst boiling 10 c.c. of a 5 per cent. solution of barium chloride is added, after which the boiling is continued for half an hour. The precipitated barium sulphate is filtered off and weighed in the usual manner and the amount calculated into sulphur.

Half-hydrated lime is made thus: Calcine a quantity of marble and divide the powder into two portions. To one of these add exactly the weight of water necessary to form $Ca(OH)_2$ and then mix with the other half.

DETERMINATION OF BENZENOID HYDROCARBONS IN COAL GAS

Pending the discovery of something better, the following methods are given. They are said to yield satisfactory results if carefully carried out.[1]

To estimate benzol or toluol in coal gas by absorption is a rather difficult test, as at least 100 cubic feet of gas should be treated, the content of these oils being so low. But the oleic acid test for light oils in gas is, as a works test, fairly reliable, and useful where a stripping plant is in use. Three bubbling bottles should be used (about 1-inch seal in each bottle) containing the oleic acid (oleic acid B.P. is used), and a convenient

[1] See *Gas World*, Coking Section, Aug. 1916, p. 13.

amount of gas, say 10 cubic feet, bubbled through. After this, the contents of the bottles should be steamed, *i.e.* steam bubbled through and condensed by passing through a suitable condenser, a measuring cylinder being provided to receive the condensate, which consists of water and light oil. The latter can be easily read off, say as c.c. per cubic foot, and can be calculated to a convenient standard, say gallons per ton of coal (4543 c.c. to a gallon). Ten to fifteen minutes should be allowed for steaming. In that time all recoverable light oil will have come over; and, of course, after a series of tests, if the oil be retained, there would be a sufficient quantity of it to fractionate in the ordinary way, separating the water by means of a separator, and the last traces by means of the addition of a little calcium chloride. The oleic acid, after separation from water as the result of the steaming, may be used again, and will last some number of tests, if a little fresh acid is added occasionally. This test is in use on several plants.

MÜLLER'S METHOD FOR THE DETERMINATION OF BENZOL, ETC., IN COAL GAS ?[1]

Müller's method consists in passing a measured volume of gas first through a washing and drying train (consisting of two bottles containing 25 per cent. caustic potash solution, one bottle with 25 per cent. sulphuric acid, and two large tubes filled with granulated anhydrous calcium chloride), and then through four weighed absorption bottles of "oleum petroleum." These are connected to a fifth empty and weighed catch-bottle, followed by a drying tube and the gas meter. Interposed between the two last-named is a pressure gauge for correction of the results to N.T.P., if this is necessary. The five weighed bottles are placed in a shallow tray and surrounded by ice. The train is connected to the gas main before the benzol scrubber inlet, and gas is passed through at a speed of 10 litres per hour. The increase in weight of the five bottles is taken as the weight of benzol, etc., in the volume of gas washed. A similar train fixed to the gas main at the scrubber outlet will indicate what amount of benzol is left in the gas, and from the two figures the scrubbing efficiency is arrived at. The test should extend over at least twenty-four hours, and be timed to correspond with the times of emptying the "benzol daily production" tank, so that actual makes can be compared with the efficiency figures. The "oleum petroleum" of the British Pharmacopœia is used. Its specific gravity should be 0.88, its boiling point 360° C., it should be non-volatile at ordinary temperatures, and should deposit no solids at 0° C.

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[1] See *Gas World*, Coking Section, February 1917, p. 19.

Wilson[1] and Bradley[2] favour the use of petroleum instead of oleic acid. The petroleum oil used must not yield anything under 200° C. when heated in a retort. Coal gas is passed through the petroleum, and the increase in weight of the petroleum after the passage of the gas is considered as benzenoid hydrocarbons, or else the petroleum is distilled after the gas has been passed through it and the distillate collected up to 120° C. (or 165° C.) is assumed to be crude benzol.

There is certainly a need for a rapid and reliable works test for benzenoid hydrocarbons in coal gas.

TESTING BENZOLISED AND DEBENZOLISED OIL FOR CRUDE BENZOL CONTENT

Two hundred c.c.'s of the oil are placed in a retort with the thermometer in the liquid. The retort is connected to a moderately long air-cooled, or a short water-cooled, condensing tube and any distillate up to 160° C. collected in a 20 c.c. graduated measure. This distillate is considered as crude benzol.

DETERMINATION OF NAPHTHALENE IN COAL GAS

Macleod and Henderson[3] recommend passing 0.7 cubic foot of gas per hour through a saturated solution of citric acid and then through a ten-bulb absorption tube containing 2.6 grammes of recrystallised picric acid and about 100 c.c. of water. At the end of the test the contents of the absorption tube are washed into a 250 c.c. flask and heated to 40° C. (104° F.) on the water-bath until all the picric acid has dissolved. After cooling, the saturated picrate is filtered off and the unused acid titrated with $\frac{N}{10}$ soda. About 10 cubic feet of gas are passed through the apparatus, the actual amount being measured by the use of a meter.

C. J. Dickenson Gair[4] gives the following method: About 350 c.c. of acetic acid (sp. gr. 1.044) are taken in two Woulff's bottles or towers. A small Woulff's bottle containing 150 c.c. of picric acid solution is also placed after the acetic acid bottles to act as a catch, and a measured volume of gas, not more than 3 to 6 cubic feet usually, passed through at the rate of about 1 cubic foot per hour. If the gas is impure a bottle containing oxalic acid solution maintained at a temperature of 80° C. is fitted in front of the bottles containing the acetic acid. In the event of there not being sufficient pressure to force the gas through the wash bottles, or if the gas be under vacuum, use is made of a piece of apparatus which pulls the gas through the bottles by means of a water pump and then automatically separates it from the water, the gas passing through the experimental meter at the ordinary atmospheric pressure. After the experiment is finished, the acetic acid and picric acid from the bottles are mixed in a flask, and about 500 c.c. of concentrated picric acid solution added. Pure naphthalene picrate separates out at once, in large flocculent masses, which have the advantage of being extremely easy to filter. After filtering, the naphthalene picrate is dried *in vacuo* or in a warm room, and weighed.

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[1] *Gas World*, Coking Section, Dec. 2, 1916, p. 11.

[2] *Gas World*, Coking Section, Jan. 6, 1917, p. 9.

[3] "Notes on Naphthalene in Coal Gas," *J.S.C.I.*, 1914, p. 299. Also *J.S.C.I.*, 1913, p. 76.

[4] *J.S.C.I.*, 1905, p. 1279.

DETERMINATION OF THE PERCENTAGE OF BENZENE, TOLUENE AND XYLENE IN COMMERCIAL TOLUOL, AND THE ANALYSIS OF CRUDE BENZOL FROM COAL GAS, ETC., ONLY CONTAINING NEGLIGIBLE AMOUNTS OF PARAFFINS

BY H. G. COLMAN, D.Sc., Ph.D.

Through the great courtesy of Dr H. G. Colman the writer is enabled to place before his readers these methods of analysis in full:

In devising a test for the determination of the amount of the three main constituents of commercial toluol, namely, toluene with benzene and xylene, the object aimed at has been to work out a test complying as far as possible with the following conditions:

(1) The results obtained should have a reasonable degree of accuracy.

(2) The time required for carrying out the test should be as short as possible, consistently with fair accuracy of results.

(3) The apparatus employed in the test should be such as can be obtained readily.

As the result of a large number of distillations of varying mixtures of known amounts of pure benzene, toluene, and xylene, carried out in an ordinary Wurtz distilling flask, it was found that if the distillation is carried out under uniform conditions, it is possible to ascertain with reasonable accuracy the percentage composition of these mixtures by the determination of the fractions (*a*) boiling below 104.7° C. and (*b*) boiling above 115.9° C. Further experiments with similar mixtures of pure benzene, toluene, and xylene, but also containing small quantities of the other substances often present to a limited extent in commercial toluol, such as carbon bisulphide and cumenes, showed that the presence of these does not materially influence the results obtained. A table constructed from the results obtained with the mixtures of pure benzene, toluene, and xylene may therefore be employed with reasonable accuracy in the determination of the percentage of these constituents in commercial toluol *which has been properly washed with caustic alkali and sulphuric acid* to remove phenols and unsaturated compounds, this being distilled under the same conditions as were employed with the pure mixtures and the percentages boiling below 104.7° and above 115.9° ascertained.

The presence of paraffin hydrocarbons of similar boiling point affects the results of the tests, but an approximate correction on this account for quantities of paraffins not exceeding 4-5 per cent. of the whole may be obtained from the specific gravity of the distillates.

In the diagram, page 262, drawn up from the results of a series of tests with mixtures of known composition, the percentages boiling below 104.7° are given in order horizontally from left to right, and the percentages above 115.9° vertically from bottom to top. The percentage of benzene is found by noting the point vertically above the figure giving the percentage below 104.7°, and on a horizontal line with the figure showing the percentage above 115.9°. From the position of this point with regard to the series of curves in broken lines, and numbered 13 to 35, the percentage of benzene in the sample may be read off. In the same manner from the position of this point with regard to the series of curves in full lines, and numbered 50-75, the percentage of toluene in the sample may be read off. The percentage of xylene is found by taking the difference between the sum of the percentages of benzene and toluene and 100.

The diagram only holds good generally for samples containing from 50-75 per cent. of toluene, and for such as give at least 5 per cent. and not more than 50 per cent. either below 104.7° or above 115.9°. In the great majority of cases the commercial samples fall within the limits named, but by a simple modification, the exceptional samples can also be analysed in a similar manner.

Mode of Carrying out the Test

Apparatus

A standard Engler 100 c.c. distillation flask, as employed in the petroleum industry, having the following dimensions:

Internal diameter of bulb	6.5 centimetres.
Length of neck	15.0 ,,
Internal diameter of neck	1.6 ,,
Length of side tube	10.0 ,,

Vertical height of side tube above surface of liquid when flask is charged with 100 c.c. . . .	9.0 centimetres.
Angle of side tube	75.0 degrees.

Round-bottomed flask of 150-200 c.c. capacity.

A Young 12-bulb "pear" fractionating column or other efficient column.

Efficient water-cooled condenser, perferably a 10-inch Liebig condenser with four bulbs blown on inner tube and placed vertically. Connection with distillation flask may be made by an adapter, or by fusing an additional length of glass tubing on to the side tube of flask, and bending to fit upper end of condenser.

Set of 100 c.c. graduated cylinders.

Thermometer registering from 50-150° C. and graduated in $\frac{1}{5}$th degrees.

Correction of 100 *c.c. Cylinders.*—The graduations of the 100 c.c. cylinders sold are sometimes incorrect to the extent of 1 c.c. The cylinders employed must be standardised by running into them known quantities of liquid, preferably toluene, from an accurate burette.

Correction of Thermometer for Barometric Pressure.—Each day before testing, the correction for barometer must be ascertained by placing the thermometer in a distillation flask with the bulb just below the side tube, and boiling distilled water in the flask. The difference between the observed thermometer reading and 100° (Nat. Phys. Lab. Standard) is taken as the correction of the thermometer for that barometric pressure. Thus if the water is found to boil under these conditions at 99.4°, and the thermometer registers correctly as regards scale graduation at 100°, then 100 — 99.4° = .6° must be *deducted* from the readings of that thermometer corresponding to 104.7° and 115.9° (N.P.L. Standard) to obtain the actual points of interruption of the distillation to be employed at that barometric pressure to be equivalent to 104.7° and 115.9° corrected (N.P.L. Standard). If the water is found to boil at 100.2°, then 100.2°—100 = 0.2° must be *added* to the readings corresponding to 104.7° and 115.9°.

If the thermometer is not correctly graduated at 100°, then the correction is found by taking the difference between the observed boiling point of distilled water in a distillation flask and the reading of the thermometer corresponding to 100° N.P.L. Standard. Thus if the observed boiling point of distilled water in the Wurtz flask is 99.4° and the scale graduation of 100.4° on that thermometer corresponds to 100° (N.P.L. Standard) then 100.4 — 99.4 = 1.0° must be deducted from the readings of that thermometer corresponding to 104.7° and 115.9° (N.P.L. Standard).

Standardising of Thermometer.—The thermometer used should be standardised (with scale fully immersed) to the National Physical Laboratory Standard, and the necessary scale corrections made.

If a thermometer has to be used the scale correction of which is unknown, this may be standardised for the purposes of this test in the following manner:

A mixture of pure benzene, toluene and xylene in known proportions is made up (one containing 20 per cent. of benzene, 65 per cent. of toluene and 15 per cent. of xylene forms a convenient composition). From the diagram, it will be seen that 100 c.c. of such a mixture should give 22.7 c.c. distilling up to 104.7° corr. and 20.5 c.c. residue at 115.9° corr., and the fraction 104.7–115.9° should be 100—22.7—20.5 = 56.8 c.c.

100 c.c. of the mixture is then distilled in the manner specified above and the temperature on that thermometer ascertained and noted at which (after draining) 22.7 c.c. have distilled over. The distillation is then continued, and the temperature ascertained and noted at which (after draining) a further 56.8 c.c have distilled over. The two temperatures thus ascertained represent the actual temperatures to be employed as interruption points of the distillation, with that thermometer and at that barometric pressure. The correction for barometer, etc., at that time is determined by placing the thermometer in a distillation flask with the bulb just below the side-tube, and boiling distilled water in the flask, the necessary correction being the difference between the reading thus found and 100°. This difference, added to each of the temperatures found as above, gives the actual corrected temperatures to be employed as interruption points for the distillation with that thermometer, equivalent to 104.7° and 115.9° corrected N.P.L. Standard.

Thus, for example, if it is found with a thermometer that with the above mixture the temperatures required to give 22.7 c.c. of the first fraction and 56.8 c.c. of the second fraction are 104.0° and 115.7° respectively, and that the boiling point of distilled water at the same time is found to be 99.5, then the actual corrected temperatures to be employed when using this thermometer to correspond to 104.7° and 115.9° corrected, N.P.L. Standard, are 104.0 + 0.5° and 115.9 + 0.5 = 104.5° and 116.4° respectively. These are then taken as the corrected distillation interruption temperatures for this thermometer, the barometer correction for the day being taken in the manner prescribed above.

The correctness of these temperatures should then be tested by making two or three mixtures of different proportions of benzene, toluene and xylene, and subjecting these to the test, and seeing whether the results obtained agree substantially with the actual percentages of benzene, toluene and xylene taken.

Any thermometer used for making the test, even when the graduation has been standardised, should first be tested with a mixture of known amounts of pure benzene, toluene and xylene, as it has been found in a few instances that thermometers which are perfectly correct in their graduation do not give correct results. So far as at present ascertained, this appears to be due in some way to the composition of the glass used in making the thermometer, which causes a "lag" in the readings of the thermometer when in vapours of low latent heat such as benzene and toluene.

In order to check the whole apparatus, thermometer and method of working, it is advisable occasionally, after making an analysis of a toluol of unknown composition, to make up a mixture of benzene, toluene and xylene in the proportions found by the test in that sample, and put this mixture through the test; if all is in order, the percentages of benzene, toluene, and xylene found by the test to be present in the check mixture should substantially agree with the actual percentages taken.

Method of Distillation

Engler 100 c.c. distillation flask and condenser to be washed out with the toluol to be tested and allowed to drain.

100 c.c. of the toluol (the temperature of which is taken) to be tested is poured into flask from graduated cylinder, the latter being drained out only.

Small naked flame under flask with wire gauze screen to protect flame and bulb of flask from draughts.

Top of thermometer bulb just below side tube of distillation flask.

Rate of distillation 7 c.c. per minute from end of condenser, the distillates being collected in 100 c.c. cylinders.

When the thermometer reaches 104.7° C. (corrected) the heating is stopped, the condenser allowed to drain, and the receiver changed; the distillation is continued till the thermometer reaches 115.9° C. (corrected). The heating is then stopped, the condenser allowed to drain, and the residue in the flask, after complete cooling, drained into a 100 c.c. cylinder. The number of c.c. distilling (1) below 104.7°, (2) between 104.7 and 115.9°, and (3) above 115.9° are read off at a temperature approximating to that found for the original sample when measuring out the 100 c.c. taken for analysis. The combined amounts of the three distillates should not amount to less than 99.5 c.c.

From the amounts boiling (*a*) below 104.7° and (*b*) above 115.9° the percentage of benzene and toluene in the sample is found, subject to the correction for paraffin content specified below, by means of the diagram.

Thus if the percentage found below 104.7° is 39, and that above 115.9° is 13, the percentage of benzene in the sample is 25.0, and that of toluene 65.0, and that of xylene, found by difference from 100, is 10.0.

The diagram only holds good for samples containing 50-75 per cent. of toluene, and for those which contain such amounts of benzene and xylene as yield not less than 5 per cent., or more than 50 per cent. either below 104.7° or above 115.9°.

In cases where a sample does not fall within these limits the analysis may be made in the following modified manner:

A measured amount of the sample less than 100 c.c. is taken and made up to 100 c.c. by the addition of such measured volumes of pure benzene, toluene, or xylene that the resulting mixture comes within the specified limits. The percentages of benzene and toluene in this mixture are then ascertained in the manner specified above, and from these percentages are deducted the volumes of benzene and toluene (if any) which have added to make up the 100 c.c. The figures thus obtained give the number of c.c. of benzene and toluene contained in the volume of the original sample taken for analysis, and the percentages in this sample are found by multiplying these figures by 100 and dividing by the volume taken.

The benzene employed for such addition should distil within a range of about 0.5°, and have a sp. gr. of 0.883-0.885 at 15.5°, and the toluene should boil within a range of 0.5° and have a sp. gr. of 0.870 at 15.5°. The xylene ordinarily obtainable, being a mixture of several isomerides, has no constant boiling point, but should distil within a range of 138-143° C. corr.

The volume of the sample it is desirable to take, and the amounts of benzene, toluene, or xylene to be added, may be judged from the results of the first distillation. Examples are given below of the proportions actually adopted in the case of typical samples not falling within the limits of the diagram.

(1) The percentage of the sample boiling *either* below 104.7° *or* above 115.9° may be below 5.

In this case 90 c.c. only of the sample is taken, and mixed previous to distillation with 10 c.c. of pure benzene if in the first test the distillate below 104.7° has been found less than 5 per cent., or with 10 c.c. of xylene if the amount boiling above 115.9° has been found below 5 per cent.

Thus if the first test showed less than 5 per cent. below 104.7°, and a mixture of 90 c.c. of the sample with 10 c.c. of benzene gave 10 per cent. below 104.7° and 17 c.c. above 115.9°, the percentage of benzene in the mixture is found from the diagram to be 15 and that of toluene 74. As 10 c.c. of benzene was added and no toluene, the 90 c.c. of the original sample contains 15 − 10 c.c. = 5 c.c. of benzene and 74 c.c. of toluene, and the percentage of benzene, toluene, and xylene in the original sample is as follows:

$$\text{Benzene} = \frac{5 \times 100}{90} = 5.5 \text{ per cent.}$$

$$\text{Toluene} = \frac{74 \times 100}{90} = 82.2 \quad ,,$$

$$\text{Xylene, by difference} = 12.3 \quad ,,$$

(2) The percentage boiling *both* below 104.7° *and* above 115.9° may be so low that there is no corresponding entry in the diagram.

In this class, which includes samples containing high percentages of toluene, 80 c.c. of the original sample may be taken and mixed with 10 c.c. of pure benzene and 10 c.c. of pure xylene, and the percentage of benzene and toluene in the mixture determined as above. The percentage of benzene thus found, less the 10 c.c. of benzene added, multiplied by 100 and divided by 80, gives the percentage of benzene in the original sample, and that of toluene without deduction, also multiplied by 100 and divided by 80, gives the percentage of toluene in the original.

Thus if a mixture of 80 c.c. of a sample with 10 c.c. of benzene and 10 c.c of xylene showed the presence of 14 per cent. of benzene and 74 per cent. of toluene, the original 80 c.c. contained 14 − 10 c.c. = 4 c.c. of benzene and 74 c.c. of toluene, the percentage of benzene is 5.0, that of toluene 92.2, and the xylene by difference 2.8.

(3) The percentage boiling above 115.9° may be so high that there is no corresponding entry in the diagram.

In this class 80 c.c. is taken and mixed with 20 c.c. of benzene previous to distillation. The figure found for percentage of benzene in the mixture less the 20 c.c. added, and the toluene figure without deduction, multiplied by 100 and divided by 80, give the percentages of benzene and toluene in the original sample.

(4) The percentage boiling below 104.7° may be so high that there is no corresponding entry in the diagram.

In this class, which comprises samples containing relatively high percentages of benzene and low percentages of toluene, 80 c.c. of the sample is mixed with 20 c.c. of pure toluene. The figure found for percentage of benzene in the mixture, without deduction, and the toluene figure, less the 20 c.c. added, give the amount of benzene and toluene contained in 80 c.c. of the sample.

Thus if 80 c.c. of a sample mixed with 20 c.c. of pure toluene, showed as the result of the distillation of the mixture the presence in the latter of 29 per cent. of benzene and 58 per cent. of toluene, the number of c.c. of benzene in 80 c.c. of the original sample is 29 and that of toluene 58 − 20 = 38 c.c., and the percentage composition of the sample is 36.2 per cent. benzene, 47.5 per cent. toluene, and (by difference) 16.3 per cent. xylene.

Correction for Paraffin Content of Toluene in Government Toluol Contracts

In the case of Government contracts for the supply of commercial toluol, the correction for paraffin content, which is only required on the percentage of toluene, is made in the following manner:

100 c.c. of the sample is placed in a round-bottomed flask of 150-200 c.c. capacity, fitted with a suitable fractionating column such as a Young 12-bulb "pear" column and distilled at the rate of about 4 c.c. per minute from the end of the condenser. The fraction distilling between 107-115° (corrected) is collected separately, and its specific gravity at 15.5° C. ascertained by any method giving results accurate to the third place of decimals. For every 0.001 that the specific gravity is found below 0.868, a reduction at the rate of $\frac{3}{4}$ per cent. is to be made on the amount of toluene found by the distillation test.

Thus if the percentage of toluene found by the distillation test is 70, and the specific gravity of the fraction 107-115° obtained in the prescribed manner is 0.864 at 15.5°, $4 \times \frac{3}{4} = 3$ per cent. of the figure shown by the distillation test is to be deducted. The corrected percentage of toluene, allowing for paraffin content, is therefore 70 − 3 per cent. of 70 = 70 − 2 = 68 per cent.

Correction of both Benzene and Toluene Percentages for Paraffin Content in Commercial Toluol

When the mixture of benzene, toluene, and xylene is to be analysed for both benzene and toluene content, and contains also moderate amounts of paraffins (4-5 per cent.), an approximate correction for these may be made as follows:

The distillation of 100 c.c. of the sample is carried out in the manner already described, and the percentages boiling below 104.7°, between 104.7-115.9°, and above 115.9° ascertained, and in addition the sp. gr. of the fractions below 104.7° and between 104.7-115.9° determined at 15.5° C. by any method giving results correct to the third decimal place. If the temperature is above or below 15.5° C., the result may be corrected to that temperature by adding 0.0009 for each degree *above* or deducting 0.0009 for each degree *below* 15.5°. The "uncorrected" percentages of benzene and toluene are then ascertained by means of the diagram. For each 0.001 that the sp. gr. of the fraction below 104.7° is found less than 0.873, a reduction at the rate of 1.0 per cent. is to be made on the "uncorrected" percentage of benzene, and for each 0.001 that the sp. gr. of the fraction 104.7–115.9° is found below 0.870, a reduction at the rate of ⅔rds per cent. is to be made on the "uncorrected" percentage of toluene.

Thus, for example, the distillation of 100 c.c. of a sample of commercial toluol containing paraffins gave the following results:

Below 104.7° .	29.8 per cent.	sp. gr. at 15.5° = 0.864
104.7–115.9° .	47.6 ,,	sp. gr. at 15.5° = 0.867
Above 115.9° .	22.5 ,,	

From the diagram the uncorrected percentages of benzene and toluene are:

Benzene	23.5 per cent.
Toluene	60.0 ,,

The sp. gr. of the fraction below 104.7° being 0.864 or 9 in the third decimal place below 0.873, and that of the fraction 104.7–115.9° 0.867 or 3 in the third decimal place below 0.870, the corrected percentages are found as follows:

Benzene

	Per cent.
Benzene, uncorrected . . . . . =	23.5
Paraffin correction 9 × 1 = 9 per cent. of 23.5 per cent. . . . . . . =	2.1
Benzene, corrected for paraffins . . . =	21.4

Toluene

	Per cent.
Toluene, uncorrected . . . . . =	60.0
Paraffin correction $3 \times \frac{2}{3} = 2$ per cent. of 60 per cent. . . . . . . =	1.2
Toluene, corrected for paraffins . . . =	58.8

Removal of Carbon Bisulphide

The small amounts of carbon bisulphide sometimes present in commercial toluol do not materially affect the results. In the case of products which contain large amounts of benzene, such as 50/90's benzols, this impurity is often present in considerable quantity and must be removed before analysis by the above method.

For this purpose, 250 c.c. of the sample is placed in a separating funnel, 30 c.c. of a 10 per cent. alcoholic solution of caustic soda or 10 per cent. alcoholic sodium ethylate added, and the whole well shaken, after which 100 c.c. of water is added with renewed shaking. After settling, the lower layer is run off, and the oil washed twice with successive quantities of 20 c.c. of water, the washings being added to the alcoholic soda extract. The oil is then dried for thirty minutes with a little anhydrous calcium chloride, filtered into a 250 c.c. flask through a small amount of cotton wool placed in the stalk of a funnel, the drying material and filter being washed with sufficient pure xylene to make up the volume to 250 c.c.

(The alcoholic caustic soda or sodium ethylate may be made with ethyl alcohol, or with "industrial" methylated spirit, but not with ordinary methylated spirit, as the latter contains paraffins.)

The oil thus treated represents the original sample, except that the carbon bisulphide in it has been replaced by xylene, and the determination of the percentage of benzene and toluene may be made in the manner already described. The difference between the combined percentages of benzene and toluene and 100, however, no longer gives the percentage of xylene, but that of xylene+carbon bisulphide in the original sample.

If an estimation of the carbon bisulphide is required, this may be made as follows: The combined alcoholic soda extract and washings are boiled to drive off alcohol, cooled and made up to 250 c.c. 25 c.c. of this solution (containing therefore the carbon bisulphide present in 25 c.c. of the sample) is boiled with 3-4 grammes of sodium peroxide, which converts the sulphur of the carbon bisulphide into sodium sulphate. The solution is then made slightly acid with hydrochloric acid, filtered, and the sulphur determined as barium sulphate in the usual manner. The weight of barium sulphate found multiplied by 0.163 gives the number of grammes, or multiplied by 0.128 the number of c.c., of carbon bisulphide present in 25 c.c. of the sample, and these figures multiplied by 4 give respectively the number of grammes of CS_2 per 100 c.c. and percentage by volume of the carbon bisulphide in the original sample.

Analysis of Unwashed Commercial Toluol

In the case of a sample of toluol which has not been previously freed from unsaturated compounds and phenols, these must be removed before analysis. For this purpose 250 c.c. of the sample are placed in a separating funnel, and shaken for

5 minutes with 20 c.c. concentrated sulphuric acid, and allowed to settle for 15 minutes. The acid layer is then run off, and the residual oil washed successively with 20 c.c. of 10 per cent. aqueous caustic soda and 20 c.c. of water. If carbon bisulphide is also present in more than small amount, this is also removed by means of alcoholic caustic soda in the manner already described. The oil is then dried for 30 minutes with a little anhydrous calcium chloride, and filtered through a small amount of cotton wool placed in the stalk of a funnel, the drying material and filter being washed with 2 to 3 c.c. of pure xylene and the filtered oil distilled, using good column, up to 140° C., collecting the distillate in a 250 c.c. flask. The contents of the latter are made up to 250 c.c. with pure xylene, and well mixed by shaking.

The oil thus obtained represents the original sample, except that the unsaturated compounds, phenols, and carbon bisulphide have been replaced by xylene, and the determination of the percentage of benzene and toluene is then carried out as already described. Here also the difference between the combined percentages of benzene and toluene and 100 no longer gives the percentage of xylene, but that of xylene+impurities.

Unsaturated Compounds, &c., in Washed Commercial Toluol

90 c.c. of a sample of washed commercial toluol, when shaken for 5 minutes with 10 c.c. of 90 per cent. sulphuric acid, should not impart more than a light brown colour to the acid layer.

Comparative Quantitative Test for Amount of Unsaturated Compounds present in Commercial Benzol, Toluol, etc.

A comparative quantitative indication of the extent to which a sample of washed commercial benzol, toluol, or solvent naphtha still contains impurities such as unsaturated compounds and thiophen derivatives, may be obtained by determination of the amount of oxygen it will absorb from potassium permanganate under specified conditions, as follows:

80 c.c. of water and 10 c.c. of dilute sulphuric acid (made by adding 1 part by weight of concentrated sulphuric acid to 3 parts by weight of water) are placed in a stoppered bottle of about 300 c.c. capacity, to which 10 c.c. of the sample of benzol, toluol, or solvent naphtha is added, and the whole shaken.

The temperature of the liquid should be maintained at as near 15° C. as practicable and should not exceed 25°.

50 c.c. of decinormal permanganate solution is then added, and the whole shaken continuously for exactly three minutes; if, at the end of half a minute, the permanganate solution is

markedly decolorised, a further 50 c.c. of decinormal permanganate is added and the shaking then continued for a further 2½ minutes. The excess of permanganate is then immediately destroyed by the addition of 10 c.c. of a 10 per cent. solution of potassium iodide, with vigorous shaking.

The resulting solution containing iodine is then titrated with decinormal sodium thiosulphate solution, shaking well between each addition, until both layers in the bottle become completely colourless. The end-point of the titration is sharply indicated by the final disappearance of the violet colour of the benzene layer, and there is no necessity to add starch as indicator.

The number of c.c. of thiosulphate solution required for the titration is deducted from the volume of permanganate solution taken, the difference giving the number of c.c. of decinormal potassium permanganate solution reduced by 10 c.c. of the sample under the above conditions, and this figure gives a comparative indication of the extent to which the sample contains oxidisable impurities.

If the number of c.c. of potassium permanganate solution used is multiplied by 0.008, the resulting figure gives the number of grammes of oxygen absorbed from permanganate by 100 c.c. of the sample.

Analysis of Crude Benzol from Coal-gas or Analogous Products consisting chiefly of Benzene, Toluene in smaller Proportion, and still smaller Proportions of Solvent and Heavy Naphtha Constituents.

The sp. gr. of the sample is taken and recorded. (Specific gravities throughout are to be given at 15.5° C. or 60° Fahr. compared with water at 15.5° C. or 60° Fahr. Correction for temperature 0.0009 for each degree C. or 0.0005 for each degree Fahr.)

250 c.c. of the sample are distilled from a round-bottomed flask (preferably of metal) fitted with a Young 12-bulb "pear" column (or other efficient column the contents of which drain out completely), and the distillate to 170° C. collected and measured, the rate of distillation being about 4 c.c per minute.

Loss on Alkali Washing.—The distillate is well shaken with 50 c.c. of 10 per cent. aqueous caustic soda, allowed to settle, the caustic layer run off, the oil washed with 20 c.c. of water, and the residual oil measured. The loss of volume is taken as the loss on alkali washing, and calculated as percentage of the original oil.

Loss on Acid Washing.—The oil after alkali washing is shaken with 8 per cent. of its volume of concentrated sulphuric acid for five minutes, allowed to settle for fifteen minutes, and the residual oil washed successively with water, 20 c.c. of 10 per cent. aqueous caustic soda, and finally with 20 c.c. of water. The volume of washed oil is measured, and the additional loss of volume taken as loss on acid washing and calculated as percentage of the original oil.

(If the loss on alkali washing and acid washing are not required separately, the washing with 50 c.c. of caustic soda solution is omitted, and the washing carried out direct with 8 per cent. of concentrated sulphuric acid, alkali and water, as under "loss on acid washing." In that case, the observed loss is "loss on acid and alkali washing.")

The washed oil is dried with calcium chloride for 30 minutes, then filtered through a little cotton-wool placed in the stalk of a funnel, the drying material and filter being washed out with 2-3 c.c. of xylene.

The dried oil is then redistilled, using a Young 12-bulb "pear" or other efficient column, at the rate of about 4 c.c. per minute, and the following fractions collected: –

(1) Fraction up to 90°.
(2) Fraction 90-140°.
(3) Fraction 140-170°.
(4) Residue at 170°.

Fractions (1), (2) and (4) are measured, but the fraction 140-170° is neglected, as this contains most of the xylene added for washing out the calcium chloride, and the volume of this fraction is taken as the difference between the sum of the volumes of (1), (2) and (4) and the volume of oil after alkali and acid washing.

NOTE.—With samples which only contain small amounts of xylene, etc., the thermometer in the above distillation may not reach 140°. In that case more xylene is added to the residue in the flask, and the distillation continued to 140°, the determination of fractions (3) and (4) being in that case omitted. This addition of xylene must *not* be made *before* the fraction "up to 90°" has been collected.

Fractions (1) and (2) are then further examined as follows:—

(1) Fraction up to 90°.

The first fraction, obtained under the specified conditions, consist of benzene and toluene only, together with small amounts of carbon bisulphide and paraffins, if these were present in the original sample. These, if present and to be allowed for, are estimated in the manner described later.

Assuming their absence, in order to determine the percentages of benzene and toluene in this fraction, this is distilled in the

Engler standard flask prescribed in the "Commercial Toluol" test at the rate of 7 c.c. per minute, and the percentage boiling up to 85° (corr.) ascertained. (When the total volume of the fraction exceeds 100 c.c., only 100 c.c. of it is taken for the analysis.)

From the percentage boiling up to 85° (corr.), the percentage of toluene is found by means of a graph, which is best worked out for the actual thermometer and apparatus used by distilling in it the following mixtures :—

	Pure Benzene.	Pure Toluene.
(1)	97 c.c.	3 c.c.
(2)	94 c.c.	6 c.c.
(3)	90 c.c.	10 c.c.
(4)	85 c.c.	15 c.c.
(5)	80 c.c.	20 c.c.

From the percentage of these known mixtures boiling up to 85° (corr.), a graph is plotted out with the percentage of toluene as ordinates and the percentage of distillate to 85° at abscissæ; and this graph can then be employed for finding the percentage of toluene and (by difference) of benzene in an unknown mixture of the two from the percentage distilling up to 85°. Working in this manner, errors due to incorrect graduation of the thermometer are eliminated.

Note.—In drawing up the graph, some temperature other than 85° may be adopted if desired, such as 90°, but for percentages of toluene such as are found in the fraction "up to 90°" from crude benzols (mostly from 5-10 per cent.), 85° is a convenient temperature. The essential point is that the temperature of interruption employed in the analysis is the *same* as that used in the tests of known mixtures for plotting out the graph).

The correction of the thermometer for barometer and unheated stem may be made according to the tables given by Northall-Laurie (*Analys.*, 1915, p. 388), or the approximate correction given in the "Commercial Toluol" test may be employed. In this the boiling point of distilled water given by the thermometer is taken in a Wurtz flask, with top of thermometer bulb just below side tube of flask. The amount by which this figure is below (or above) the temperature shown by this thermometer as the boiling point of water at normal barometer with stem completely heated (100° if thermometer is correctly graduated) gives the correction for barometer and unheated stem at the then barometric pressure, and this figure must be deducted from (respectively added to) 85° to find the actual temperature to be used on that thermometer at the then barometric pressure.

Fraction 90-140°.

This fraction, obtained under the conditions specified, conists of benzene, toluene and xylene only, together with any araffins of similar boiling point which may be present in the riginal. The estimation and allowance for the latter, when resent, is considered later.

Assuming for the present their absence, the amount of enzene, toluene and xylene present is determined as follows :—

40 c.c. of the fraction (or the whole of it if there is less than 0 c.c.) is mixed with 50 c.c. of pure toluene, and made up to 00 c.c. with pure benzene, and the percentage of benzene, oluene and xylene in this mixture found by the method prescribed in the examination of Commercial Toluol, pages 262 to 269. The percentage of benzene found, less the volume of benzene added, and the percentage of toluene less the volume of toluene added, and the percentage of xylene without deduction, give the number of c.c. of benzene, toluene and xylene contained in the 40 c.c. (or smaller quantity) of the fraction taken, and from these the amount of the three constituents in the total volume of the fraction and in 100 is found by proportion.

The amounts of benzene and toluene found respectively in the two fractions "up to 90°" and "90-140°" are then added together, giving the total amount of each in the 250 c.c. originally taken, and these figures multiplied by 0.4 or divided by 2.5 give the percentages of benzene and toluene in the sample, assuming that carbon bisulphide and paraffins are absent.

Fraction 140-170°.

This fraction, found by difference, consists of constituents of solvent and heavy naphtha. To this volume is added the total number of c.c. of xylene, found in fraction 90-140°, the sum of the two giving an approximate estimation of the volume of the solvent and heavy naphtha in the crude benzol, and this volume, multiplied by 0.4 or divided by 2.5, gives their percentage of the original.

Fraction above 170°.

This fraction consists of high boiling substances which cam over with the distillate to 170° of the original oil, plus hig boiling substances formed by the action of concentrated sulphur acid on the unsaturated compounds present in the crude dis tillate to 170°. The volume found multiplied by 0.4 or divide by 2.5, gives the percentage of high boiling substances in th washed distillate to 170°, calculated on the original crude benzol

Example.

(CS_2 and paraffins assumed to be absent.)

250 c.c. of a crude benzol (sp. gr. 0.898) gave 208 c.c. distillate up to 170° :—

	Per cent. of original.
Up to 170°	83.2 per cent.
Residue at 170° (by diff.)	16.8

The 208 c.c. up to 170° gave 206 c.c. after alkali washing and 190 c.c. after acid washing :—

Loss on alkali washing = 2 c.c. = 0.8 per cent. of original.
,, ,, acid ,, = 16 c.c. = 6.4 per cent. ,, ,,

The above 190 c.c. of washed oil after drying, etc., gave :—

(1) Up to 90°	126.5 c.c.
(2) 90-140°	51.0 c.c.
(3) 140-170° by difference	3.5 c.c.
(4) Above 170°	9.0 c.c.
	190.0 c.c.

Fraction up to 90°.

100 c.c. of the 126.5 c.c. gave 86.0 per cent. distilling to 85° (corr.)

Therefore from graph . Benzene = 92.1 per cent.
Toluene = 7.9
And in the whole 126.5 c.c. Benzene = 116.5 c.c.
Toluene = 10.0 c.c.

Fraction 90°-140°.

40 c.c. of the 51 c.c. of this fraction were mixed with 50 c.c. pure toluene and 10 c.c. pure benzene, and the 100 c.c. of mixture distilled in accordance with the "Toluol-test" specification, giving—

	Per cent.
Up to 105° (104.7° N.P.L.)	27.2
105-117° (104·7-115·9° N.P.L.)	63.5
Above 117° (115.9° N.P.L.)	9.0
	99·7

Therefore, there are :—

	In Mixture.	In 40 c.c. of Fraction.	In whole 51 c.c. of Fraction.	Comp. of Fraction.
Benzene .	18.8 c.c. (−10)	= 8.8 c.c.	11.2 c.c.	22.0
Toluene .	73.2 c.c. (−50)	= 23.2 c.c.	29.5 c.c.	58.0
Xylene .	8.0 c.c. (− 0)	= 8.0 c.c.	10.3 c.c.	20.0

Adding up the benzene and toluene found in the combined fractions "up to 90°" and "90-140°" and adding the xylene found in the latter fraction to the fraction "140-170" giving an approximate representation of the solvent and heavy naphtha, there are in the 190 c.c. of washed distillate and in the 250 c.c. original:—

	Benzene	Toluene.	Xylene and S and H. Naphtha.	Above 170° in washed dist.
Fraction up to 90° .	116.5	10.0	..	.. c.c.
,, 90° to 140° .	11.2	29.5	10.3	.. ,,
,, 140° to 170° .	..	..	3.5	.. ,,
,, above 170° .	..	..	..	9.0 ,,
Total in 250 c.c. of original	127.7 = 51.1%	39.5 = 15.8%	13.8 = 5.5%	9.0 c.c = 3.6%

The complete result is therefore as follows:—

Sp. gr. at 15.5 = 0.898.

	Per cent.
Benzene	51.1
Toluene	15.8
Solvent and heavy naphtha (approximate) .	5.5
Loss on alkali washing of fraction to 170° .	0.8
Loss on acid washing of fraction to 170° . .	6.4
Substances boiling above 170° in distillate up to 170° after acid washing	3.6
Fraction of original above 170°	16.8

Carbon Bisulphide and Paraffins.

When carbon bisulphide and paraffins are present they may be estimated in the above fractions of the washed distillate up to 140° as follows:—

Fraction up to 90°.

The distillate up to 85° and residue from this fraction are remixed, and the sp. gr. of the mixture at 15.5° taken and noted. It is then mixed in a separating funnel with 50 c.c. of alcohol free from paraffins, five grammes of solid caustic soda (roughly powdered) added, and the whole shaken for five minutes. (If preferred, 50 c.c. of 10 per cent. alcoholic caustic soda or sodium ethylate may be used in place of solid caustic and alcohol, but unless these solutions are freshly prepared, more trouble is experienced in the subsequent settling, in washing, owing to formation of resinous substances in the solutions on keeping.) 200 c.c. of water is then added with renewed shaking, and after settling, the lower aqueous layer is run off, the oil washed twice with successive quantities of 25 c.c. of water, and dried with calcium chloride. The sp. gr. of the dried oil is then taken accurately to the nearest third decimal place.

The percentage of toluene in this fraction has been previously ascertained (uncorrected for paraffins) by the percentage distilling up to 85° (corr.) and the sp. gr. is calculated which a mixture of this composition of pure benzene and toluene should have, the sp. gr. of pure benzene being taken as 0.885 and of pure toluene as 0.870.

From the three sp. gr.'s thus found or calculated, namely :—

Sp. gr. of original fraction to 90°,
,, ,, ,, ,, after removal of CS_2,
,, calculated for benzene and toluene mixture of the "uncorrected" composition found,

the percentage of CS_2 and paraffins can be found in the following way, the sp. gr. of CS_2 being taken as 1.27 and of the paraffins present in this fraction as 0.73.

(1) *Carbon Bisulphide.*

If CS_2 per cent. = x,
Then $1.27x + (100 - x) \times$ (sp. gr. of fraction to 90° *after* CS_2 removal) $= 100 \times$ (sp. gr. of fraction to 90° *before* CS_2 removal).

Paraffins.

If paraffins per cent. = y,
Then $0.73y + (100 - y) \times$ (sp. gr. calc. for pure benzene and toluene) $= 100 \times$ (sp. gr. of fraction after CS_2 removal).

Fraction 90-140°.

This fraction contains no CS_2, and only paraffins in addition to benzene, toluene and xylene. To determine the amount of the latter the sp. gr. of the fraction is taken to the nearest third decimal place, and in addition, the sp. gr. is ascertained by calculation that the mixture would have if paraffins were absent. For this purpose, the percentages of benzene, toluene and xylene in the fraction, uncorrected for paraffins, already found, are multiplied by the respective sp. gr.'s of pure benzene (0.885), pure toluene (0.870) and xylene (0.866), and the sum of the multiples divided by 100. The figure thus obtained gives the sp. gr. which a mixture of the pure substances would have when of given composition provided no contraction or expansion occurs on mixing them ; the average expansion in the case of mixtures of the three in the proportions usually occurring in the fraction 90-140° is, however, such as to lower the sp. gr. by 0.001 from that calculated as above. From the figures thus found, therefore, 0.001 must be deducted to give the correct sp. gr. of the mixtures of pure benzene, toluene and xylene.

From these two sp. gr. figures, namely :—

(1) Actual sp. gr. of fraction 90-140°,
(2) Calculated sp. gr. of paraffin free mixture,

and assuming the sp. gr. of the paraffin presents in this fraction as 0.74, the percentage of the latter is calculated as follows :—

If z = per cent. of paraffins,
then $0.74z+(100-z)\times$(calc. sp. gr.)$=100\times$(actual sp. gr.).

Example.

Continuing the example from p. 274 the correction for and estimation of carbon bisulphide and paraffins are as follows :—

Fraction up to 90°

Sp. gr. found for fraction before CS_2 removal = 0.883.
,, ,, ,, ,, after ,, ,, = 0.881.

Calculated sp. gr. of 92.1 per cent. pure benzene and 7.9 per cent. pure toluene

$$=\frac{92.1\times0.885+7.9\times0.870}{100}=0.884$$

Then if CS_2 per cent. $= x$, and paraffin per cent. $= y$

$$1.27x+(100-x)\times0.881=100\times0.883.$$

$$\text{or } CS_2=\frac{88.3-88.1}{1.27-0.881}=\frac{0.2}{0.389}=0.5 \text{ per cent.}$$

$$\text{and } 0.73y+(100-y)\times0.884=100\times0.8810,$$

$$\text{or paraffins}=\frac{88.4-88.1}{0.884-0.73}=\frac{0.3}{0.154}=1.9 \text{ per cent.}$$

The CS_2 and paraffins in this fraction, therefore, together amount to 2.4 per cent., so that 2.4 per cent. of the percentage found for benzene and toluene must be deducted, and the composition of the fraction up to 90° is—

	In 100 c.c.	In the total 126.5 c.c. of Fraction.
	Per cent.	Per cent.
CS_2	0.5	0.6
Paraffins	1.9	2.4
Benzene (92.1—2.4 p.c. of 92.1	89.9	113.7
Toluene (7.9—2.4 p.c. of 7.9) .	7.7	9.8
	100.0	126.5

Fraction 90-140°.

Sp. gr. of fraction found = 0.869.

Comp. of fraction (uncorr. for paraffins) *see* p. 279.

	In 40 c.c.	Per cent.
Benzene	8.8 c.c.	22.0
Toluene	23.2 c.c.	58.0
Xylene	8.0 c.c.	20.0

Therefore calculated sp. gr. for above with no paraffins determined in the manner specified

$$=\frac{22\times0.885+58\times0.870+20\times0.866}{100}-0.001=$$

$$0.873-0.001=0.872.$$

If paraffins in fraction $= z$,

$$\text{Then } 0.74z+(100-z)\times0.872=100\times0.869.$$

$$\text{Or paraffins}=\frac{87.2-86.9}{0.872-0.74}=2.3 \text{ per cent.}$$

2.3 per cent. of the "uncorrected" percentage of benzene, toluene and xylene found on p. 277 must therefore be deducted, so that the composition of fraction 90-140°, corrected for paraffin, is—

	In 100 c.c.	In total 51 c.c. of Fraction.
	Per cent.	
Paraffins	2.3	1.2 c.c.
Benzene (22—2.3 per cent. of 22) .	21.5	11.0 c.c.
Toluene (58—2.3 per cent. of 58) .	56.7	28.9 c.c.
Xylene (20—2.3 per cent. of 20) . .	19.5	9.9 c.c.
	100.0	51.0 c.c.

Adding together the CS_2, paraffin, benzene and toluene, found in the fractions "up to 90°" and "90-140°," and proceeding otherwise as given on p. 277 when paraffins are absent, there are in the original 250 c.c. of oil and in the 190 c.c. of washed distillate from it :—

Fraction of washed dist.	CS_2.	Paraffins.	Benzene	Toluene.	Xylene and S. & H. Nap.	Above 170°.
Up to 90°	0.6	2.4	113.7	9.8	—	— c.c.
90° to 140°	—	1.2	11.0	28.9	9.9	—
140° to 170°	—	—	—	—	3.5	—
Above 170°	—	—	—	—		9.0
Total in 250 c.c. of original sample.	0.6	3.6	124.7	38.7	13.4	9.0 c.c.
Per cent. of original	0.2	1.4	49.9	15.5	5.4	3.6%

The complete analysis, therefore, including the estimation of carbon bisulphide and paraffins, comes out as follows :

	Per Cent.
Carbon bisulphide	0.2
Paraffins in fraction to 140°	1.4
Benzene	49.9
Toluene	15.5
Solvent and heavy naphtha (approx.)	5.4
Loss on alkali washing of fraction to 170°	0.8
Loss on acid washing of fraction to 170°	6.4
Substances boiling above 170° in distillate up to 170° after washing	3.6
Fraction of original above 170°	16.8

To save the calculation of the percentages of paraffins and of carbon bisulphide from the observed sp. gr.'s, and also to find the calculated sp. gr. of the paraffin free mixtures graphs can be employed, which are readily plotted out.

APPENDIX

The following is a copy of a form issued by the Home Office, which should be mounted and hung in a prominent position in all tar distilleries:

FORM 939.
September, 191

FACTORY AND WORKSHOP ACT, 1901

TAR DISTILLING.

The following directions are approved by the Home Office, and are applicable to factories in which is carried on the distillation of tar for the production of naphtha, light oil, creosote oil, and pitch.

Fencing.

1. All uncovered tar reservoirs, wells and tanks, unless constructed so as to be at least three feet in height above the ground or platform, should be securely fenced, with either a brick wall or double rails, to the height of three feet.

Cleaning

2. During the process of cleaning, every tar still should be completely isolated from adjoining tar stills either by disconnecting the pipe leading from the swan-neck to the condenser worm, or by disconnecting the waste gaspipe fixed to the worm end or receiver. Blank flanges should be inserted between the disconnections. In addition, the pit discharge pipe or cock at the bottom of the still should be disconnected.

Ventilation

3. Every tar still should be ventilated and allowed to cool before persons are allowed to enter.

Inspection

4. Every tar still should be inspected by the Foreman or other responsible person before any workman is allowed to enter.

5. The inspecting Foreman on first entering any tar still or tank, and all persons employed in tar stills or tanks in which there are no cross stays or obstructions likely to cause entanglement, should be provided with a belt securely fastened round

the body, with a rope attached, the free end being left with two men outside whose sole duty should be to watch and draw out any person appearing to be affected by gas. The belt and rope should be adjusted and worn in such a manner that the wearer can be drawn up head foremost and through the manhole and not across it.

Remedy for Gassing

6. A bottle of compressed oxygen, with mouthpiece, should be kept at all times ready for use; and printed instructions as to the use of this bottle, and the method to be employed for resuscitation by means of artificial respiration, should be kept constantly affixed. A draft of such instructions is appended.

Respirators

7. A supply of suitable chemical respirators properly charged and in good condition should be kept ready for use in case of emergency arising from sulphuretted hydrogen or certain poisonous gases. (Granules of carbon saturated with a solution of caustic soda readily absorb sulphuretted hydrogen and may be used for charging respirators.)

Lights

8. The use of naked lights should be strictly prohibited in any portion of the works where gas of an inflammable nature is liable to be given off.

Safety Valve

9. Each still should be provided with a proper safety valve, which should at all times be kept in efficient working condition.

B. A. WHITELEGGE,
Chief Inspector of Factories.

HOME OFFICE,
December, 1909.

GASSING

SYMPTOMS.—The first symptoms are giddiness, weakness in the legs, and palpitation of the heart. If a man feels these he should at once move into fresh warm air, when he will quickly recover if slightly affected. He should avoid exposure to cold. He should not walk home too soon after recovery; any exertion is harmful.

FIRST AID.—Remove the patient into fresh warm air. Send for the oxygen apparatus. Send for a doctor. Begin artificial breathing at once if the patient is insensible and continue it for at least half an hour, or until natural breathing returns. Give oxygen* at the same time and continue it after natural breathing returns.

ARTIFICIAL BREATHING (Schäfer Method).—Place the patient face downwards as shown in the diagrams.

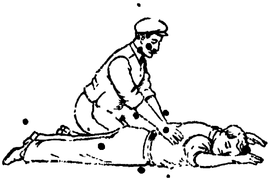

DIAGRAM 1.

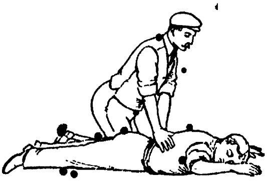

DIAGRAM 2.

Kneel at the side of the patient and place your hands flat in the small of his back with thumbs nearly touching, and the fingers spread out on each side of the body over the lowest ribs (*see* Diagram 1).

Then promote artificial breathing by leaning forward over the patient and, without violence, produce a firm, steady, downward pressure (*see* Diagram 2). Next release all pressure by swinging your body backwards without lifting your hands from the patient (*see* Diagram 1).

Repeat this pressure and relaxation of pressure without any marked pause between the movements, *about 15 times a minute,* until breathing is established.

*USE OF OXYGEN CYLINDER.—Open the valve gradually by tapping the lever key (which must first be extended to its full length) with the wrist, until the oxygen flows in a gentle stream from the mouthpiece into the patient's mouth. The lips should not be closed round the mouthpiece. The nostrils should be closed during breathing in, and opened during breathing out.

If the teeth are set, close the lips and one nostril. Let the conical end of the mouthpiece slightly enter the other nostril during breathing in, and remove it for breathing out.

The following particulars relating to sulphuretted hydrogen (SH_2), and carbon monoxide (CO), published by "Mentor" in *The Gas World* of November 21, 1908, will prove useful to those interested in tar distillation :-

Symptoms of Poisoning by Carbon Monoxide

Usually the first thing noticed by a person who is moving about and has inhaled the gas is a tendency to palpitation, dizziness or faintness and shortness of breath after exertion, following which there is a general weakening of the muscular, mental and sensory faculties. The patient is usually drowsy. When the blood has become about 50 per cent. saturated it is hardly possible for one to stand upright or walk, and with higher degrees of saturation the mental and muscular enfeeblement becomes more and more pronounced. One noteworthy point in connection with carbon monoxide poisoning is that very little actual distress results from the inhalation of the gas. After paralysis of the limbs, the senses gradually become more and more benumbed, as they would be by the administration of a gentle anæsthetic. With less than 1 per cent. of CO in the air, death is very gradual and peaceful, and with more than 1 or 2 per cent., loss of consciousness is usually followed by convulsions, and death rapidly ensues.

Symptoms Produced by Poisoning from SH_2

The symptoms produced by SH_2 poisoning are due to two causes: (1) its direct irritant action on the eyes and air passages, and (2) its intensely poisonous action, when absorbed, on the brain, heart, etc. Exposure to an atmosphere containing 0.01 to 0.02 per cent. soon produces inflammation of the eyes, and headache. Pain in the eyes often comes some time after the exposure, and with great severity, and may recur at intervals for several days. With 0.05 of SH_2, giddiness and other alarming symptoms show themselves, as well as great irritation of the eyes, nose, etc.

Tables showing the Poisonous Effects of Varying Percentages of CO and SH_2 on Human Beings

CARBON MONOXIDE

Percentage of Gas Present.				
Pure CO.	Coal Gas containing 7 per cent. CO.	Carburetted Water Gas, 30 per cent. CO.	Pure Carburetted Water Gas containing 32 per cent. CO.	Effect on Human Beings.
0.05	0.7	0.17	0.1	After half an hour to two hours, giddiness on exertion.
0.1	1.4	0.30	0.2	Do., do., inability to walk.
0.2	2.8	0.66	0.4	Do., do., loss of consciousness, and perhaps final death.
0.4	5.6	1.3	0.8	Do., do., probable death.
1.0	14.0	3.3	2.0	After a few minutes, loss of consciousness, followed before long by death.

SULPHURETTED HYDROGEN

Percentage of SH_2 Present.	Effect on Human Beings.
0.001	Strong smell of rotten eggs.
0.02	After a few minutes, irritation of the nose, throat and eyes, accompanied by coughing.
0.05	Much irritation of the eyes and throat, giddiness and headache.
0.07	Death after several hours' exposure.
0.2	Death in about one and a half minutes.

The use of Oxygen in Cases of Gassing, How it is Administered, and How Long it Should be Given

Oxygen is a valuable aid to recovery in cases of poisoning from carbon monoxide. It should therefore always be kept ready on a gasworks. The oxygen is compressed and stored in strong steel cylinders, usually holding 20 cubic feet. The cylinder should be provided with a piece of india-rubber tubing at the end of which is a metal mouthpiece. The valve on the cylinder should be opened to the extent necessary to allow sufficient oxygen to issue to allow of its being inhaled "neat," or without much admixture with air. The mouthpiece is then placed loosely in the mouth, so that inhalation may proceed without distending the lungs. If the person is unconscious, the nostrils should be closed, by pinching them with the fingers, during the process of inhaling, and left free during the act of expiration. The time during which oxygen is administered should be at least ten minutes.

DIRECTOR OF INDUSTRIES
Bengal

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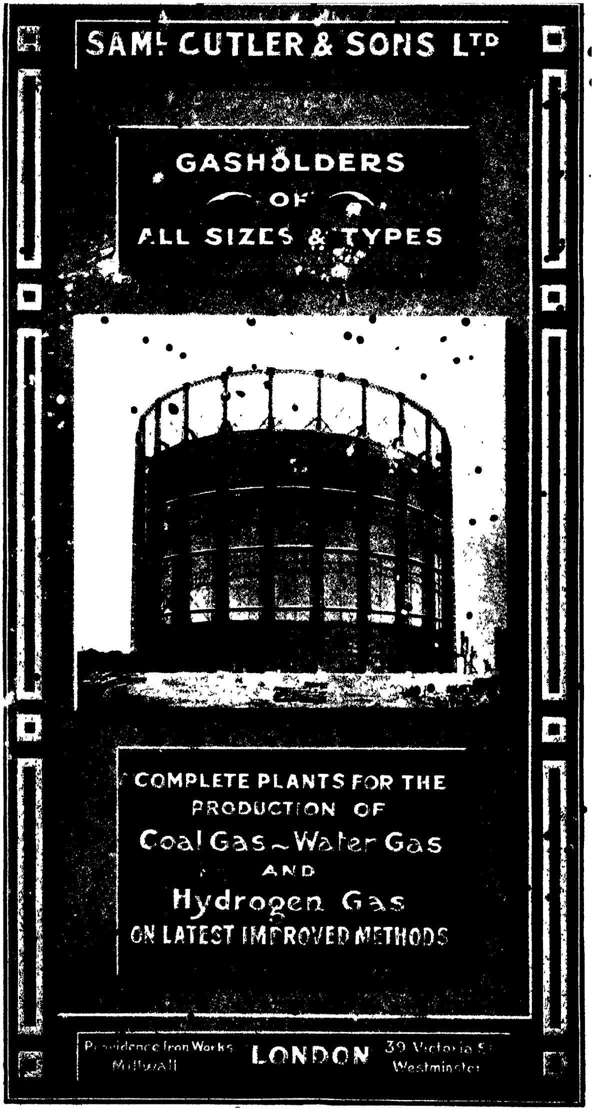

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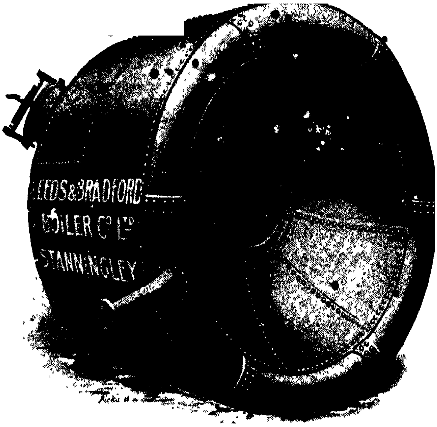

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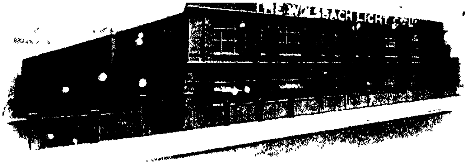

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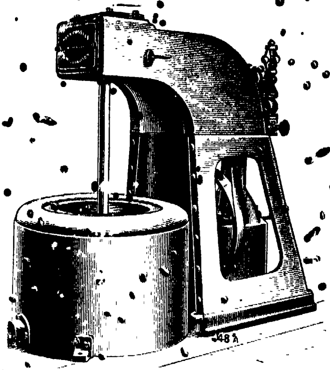

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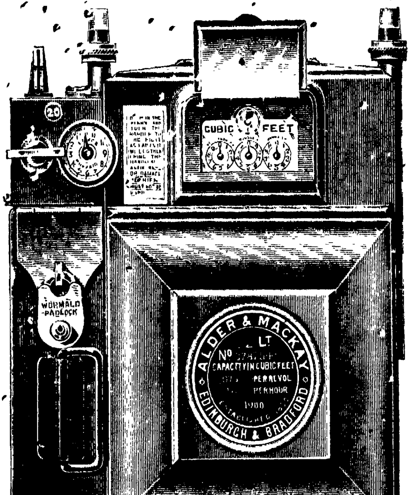

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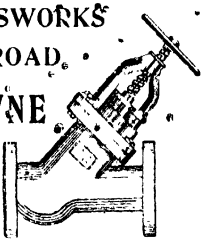

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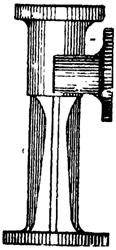

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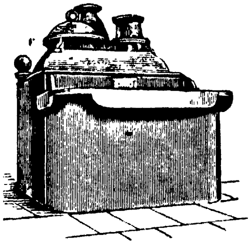

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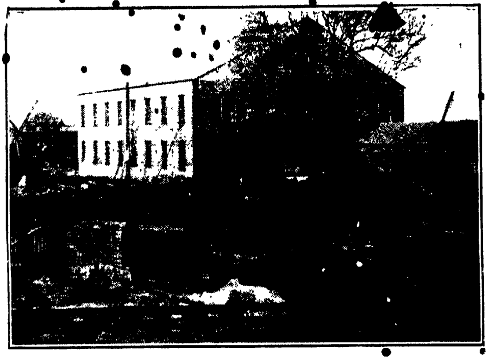

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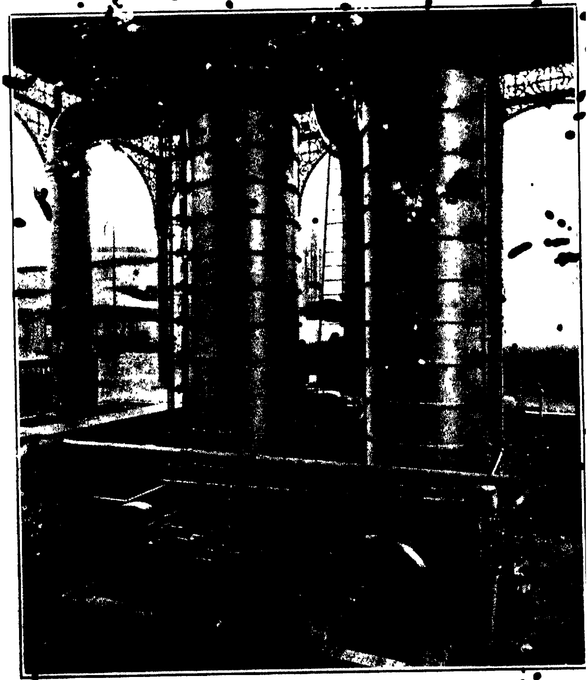

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